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　５ 年　 ６ 月 １９ 日現在

機関番号：３２６１９
研究種目：基盤研究(C)（一般）
研究期間：2020～2022
課題番号：２０Ｋ０５６８９

研究課題名（和文）Pioneering 3d transition-metals coordination polymers as novel electrocatalysts for metal-air batteries.

研究課題名（英文）Pioneering 3d transition-metals coordination polymers as novel electrocatalysts for metal-air 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）　　3,300,000円

研究成果の概要（和文）：金属空気電池の分野では、理論的に予測される高いエネルギー密度を実現するために、酸素発生反応（OER）と酸素還元反応（ORR）を高効率にサイクルできる二元機能性電極触媒が強く望まれている。 この課題に対処するために、銅およびニッケルのキレート配位ポリマー（CP）を調製し、その酸化処理で得られる複合体がアルカリ溶液中で示す OER および ORR に対する電極触媒活性とその安定性を調査した。CuCP 由来の電極触媒は主に OER に対して活性であるが、NiCP 由来の電極触媒はアルカリ溶液中で OER と ORR の両方に触媒活性を示すことがわかった。

研究成果の学術的意義や社会的意義
A new method to produce active nanocomposite electrocatalysts for oxygen evolution reaction and oxygen reduction reaction in alkaline media is proposed. The method has a potential to reduce the cost of the catalyst used in metal-air batteries and electrolyzers by replacing usage of noble metals.

研究成果の概要（英文）：In the field of metal-air batteries, a bifunctional electrocatalyst able to efficiently catalyze oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) is highly desired to provide theoretically predicted high energy densities. To address this challenge we prepared copper and nickel coordination polymers (CPs) and investigated their stability and electrocatalytic activity towards OER and ORR in alkaline solutions. It is found that CuCP-derived electrocatalyst is active mainly toward OER, while NiCP-derived electrocatalyst can catalyze both OER and ORR in alkaline solutions.

研究分野：触媒

キーワード：OER　ORR　electrocatalyst　nickel dithiooxamide　metal-air batteries　coordination polymer　copper dithiooxamide　overpotential

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

(1) Metal-air batteries ($M-O_2$) are novel, high capacity, rechargeable batteries that use a metal and oxygen from the air to generate electricity.
Fig. 1 shows general structure of $Li-O_2$ battery for aqueous type $Li-O_2$ cell. The cell consists of a lithium metal anode, polymer protective layer, electrolyte(s), and a cathode. On the discharge oxygen evolution reaction (OER), and on battery charge oxygen reduction reaction (ORR) occurs.

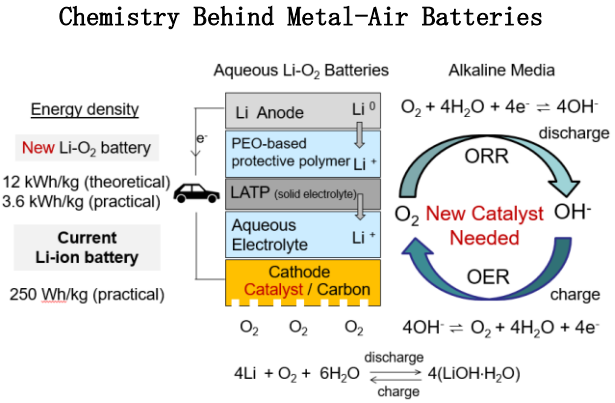

Fig. 1 Structure of aqueous $Li-O_2$ batteries.

Theoretically, $Li-O_2$ batteries can generate around 12 kWh/kg, which is close to the energy density of gasoline. With the 15 times higher energy density than the current lithium-ion batteries, such batteries could power electrical vehicles up to 500 km distance on a single charge.

(2) The challenges that limit practical application of $Li-O_2$ batteries are mostly attributed to the low efficiency of the ORR/OER processes. The efficiency of these two reactions is a bottleneck, not only in the field of $Li-O_2$ batteries, but also in the field of hydrogen generation through water splitting process. Thus, the development of active electrocatalysts for OER and ORR is of paramount importance in securing future sustainable energy sources. At present, IrO_2 and RuO_2 are used as commercial catalysts for the OER due to their low overpotential. High price of Ir and Ru metals, as well as instability of RuO_2 and IrO_2 at high anodic potentials is a major drawback that drives the development of new OER catalysts. Alkaline solutions offer a greater material choice. However, Pt which is used to catalyze ORR, show little activity in alkaline media.

The efficient electrocatalysts should have low overpotential, high stability, good electron conductivity, and fast reaction kinetics. In the case of $Li-O_2$ batteries a bifunctional electrocatalyst catalyzing OER/ORR is highly desired.

２．研究の目的

The purpose of the research is to develop a new method to obtain efficient, noble-metal free electrocatalysts for OER and ORR, working in alkaline media. To address this challenge we used transition metals coordination polymers (CPs). CPs are coordination compounds in which a metal atom, (M), is coordinated to a ligand, making a cyclic structure, and the ligand links to another metal atom, forming repeating units of coordination polymer. CPs create unique spatial architectures which are expected to serve as a template for the fabrication of catalytically active nanocomposites.

Specifically, under this research project, we aimed to synthesize copper and nickel CPs and evaluate their potential as elecrocatalysts for OER/ORR.

３．研究の方法

The following research methods were used to achieve the specific purposes of the research project;

1) Copper and nickel CPs were prepared with a dithiooxamide,(dto), as a ligand according to the synthesis method reported by Abboudi et al. Inorg. Chem. 1985, 24, 2091. The compounds were characterized by powder X-ray diffraction (XRD) and scanning electron microscope (SEM) equipped with the energy dispersive X-ray (EDX) detector used for the elemental analysis.

2) Catalyst inks were formulated by mixing CPs, carbon black and a binder in specific ratio which yielded inks with an appropriate viscosity. Screen-printed technique was applied to prepare electrodes for electrochemical tests.

3) Electrocatalytic tests were performed in 1 M KOH solutions using cyclic voltammetry (CV), linear weep voltammetry (LSV) and rotating disk electrode (RDE) methods. Before catalytic tests, electrodes were subject to potential cycling in N_2-saturated 1 M KOH solutions, a procedure which produced catalytically active oxide and oxyhydroxides nanostructures.

4) SEM-EDX and XRD was used to evaluate catalytically active species, and LSV-RDE method to understand mechanism of the reaction.

４．研究成果

The results of this study revealed a new method for fabrication of OER and ORR electrocatalysts working in alkaline solutions. The unique feature of the method is use of two-dimensional CPs as a metal template. The method can be applied to the synthesis of transition metal oxide and oxyhydroxides nanostructures and can be used in the preparation of composite electrodes for metal-air batteries and water electrolyzers. Overall, the method of electrochemical transformation of CPs in a carbon matrix has a potential to reduce the cost of the catalyst by replacing usage of noble metals.

1) In the case of copper (dto) derived catalysts, electrochemical cycling in 1 M KOH produced CuO and $Cu(OH)_2$ nanostructures (Fig. 2).

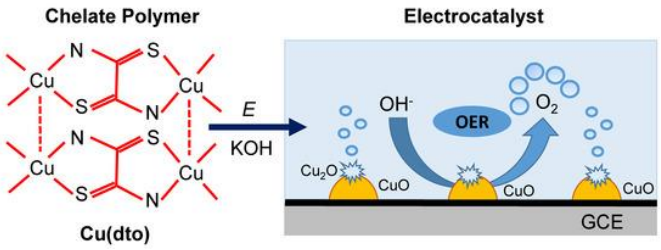

Fig. 2 Cu(dto) derived OER electrocatalyst.

The carbon-dispersed CuO nanostructures formed a nanocomposite which exhibited an enhanced catalytic activity for OER in alkaline media. The nanocomposite catalyst had and overpotential of 280 mV (at 1 mA/cm2) and a Tafel slope of 81 mV/dec in 1 M KOH solution. Per metal loading, it had a seven-fold higher current than commercially used IrO_2/C catalyst. Based on post XRD and RDE experiments, we proposed a catalytic cycle, in which CuO undergoes electrooxidation to Cu_2O_3 that further decomposes to CuO with the release of oxygen.

2) In the case of Ni(dto), electrochemical cycling in 1 M KOH resulted in the formation of γ-NiOOH (Fig. 3). While it is well-known that nickel oxyhydroxides are good OER catalysts, their catalytic activity toward ORR and catalyst phase identity was unknown.

The γ-NiOOH prepared in this study showed low overpotential not only for OER, but also for ORR. The onset potential for ORR was around 0.81 V vs. RHE, and the reaction was found to proceed via the 2e− transfer pathway. The high OER catalytic activity and relatively low ORR overpotential make this nanocomposite catalyst a good candidate for bifunctional OER/ORR catalyst for metal-air batteries.

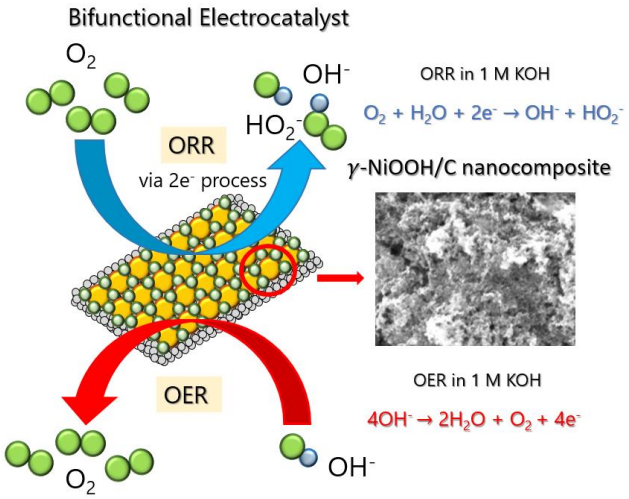

Fig. 3 Bifunctional OER/ORR electrocatalysts derived from Ni(dto).

５．主な発表論文等

〔雑誌論文〕　計5件（うち査読付論文　5件／うち国際共著　5件／うちオープンアクセス　2件）

１．著者名 Ridwan P. Putra, Ihsan Budi Rachman, Hideyuki Horino, Izabela I. Rzeznicka	４．巻 2 (4)
２．論文標題 Bifunctional Catalytic Activity of γ-NiOOH toward Oxygen Reduction and Oxygen Evolution Reactions in Alkaline Solutions	５．発行年 2022年
３．雑誌名 Oxygen	６．最初と最後の頁 479-492
掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/oxygen2040031	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 該当する

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2．論文標題 Enhanced and Heteromolecular Guest Encapsulation in Nonporous Crystals of a Perfluorinated Triketonato Dinuclear Copper Complex	5．発行年 2020年
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3．学会等名 4th International Conference on Catalysis and Chemical Engineering, Los Angeles
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〔図書〕　計0件

〔産業財産権〕

〔その他〕
Laboratory website
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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
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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