1版

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　６ 年　４ 月 ２３ 日現在

機関番号： １１３０１
研究種目： 若手研究
研究期間： 2022～2023
課題番号： ２２K１４７５７
研究課題名（和文） Topological Defect Engineering on Carbon Electrode for Advanced Batteries

研究課題名（英文） Topological Defect Engineering on Carbon Electrode for Advanced Batteries

研究代表者
ＹＵ　ＷＥＩ（YU, WEI）

東北大学・材料科学高等研究所・助教

研究者番号：１０９００９０４

交付決定額（研究期間全体）：（直接経費）　　3,600,000円

研究成果の概要（和文）：Li-02電池の正極におけるトポロジカル欠陥の触媒能を研究した．CVD法により，トポロジカル欠陥が豊富かつエッジサイトのないグラフェンメソスポンジ(GMS)を作製した．GMS正極は従来と比較し，高容量かつ優れたサイクル特性をもつ．電気化学質量分析と理論計算から，非晶質Li202に対する特異的な触媒能が3.6 V(vs. Li/Li+)の低電荷プラトーに寄与していることがわかる．加えて，これらの特性からGMSは固体触媒の担持に優れるといえる．また，自立型GMSシートは793 Wh kg-1の高いエネルギー密度と0.4 mA cm-2の実用範囲での優れたサイクル特性(>260サイクル)を示す．

研究成果の学術的意義や社会的意義
GMSの合成と活用の成功により，これまで報告されていなかったエッジサイトの影響がない，実際のLi-02電池のトポロジカル欠陥の触媒能についての知見が得られた．我々はRuを担持したGMSによってトポロジカル欠陥と固体触媒の逐次反応作用を提案した．GMSシートが示す優れた電池性能から，炭素正極の構造を適切に設計することでLi-02電池の主要な問題のほとんどを解消できると示された．Li-02電池の問題点であったエネルギー密度とサイクル特性は適切に設計された炭素電極により解消された．この結果から，電気自動車用の高いエネルギー密度をもったLi-02電池の実用化が促進されると期待される．

研究成果の概要（英文）：In this research, we investigated the catalytic effect of topological defects in carbon cathodes on Li-02 batteries for the first time. In brief, topological-defect-rich and edge-site-free graphene mesosponge (GMS) was synthesized by chemical vapor deposition. Compared with conventional carbons, the GMS cathode shows larger capacity and better cycling stability in Li-02 batteries. In situ isotopic electrochemical mass spectrometry and theoretical calculations reveal the unique catalysis of topological defects in the formation of easily-decomposable amorphous Li202, contributing to a low charge plateau around 3.6 V (vs. Li/Li+). In addition, GMS with abundant topological defects and a large surface area proved to be a good substrate for uniform loading of solid catalyst. Finally, the free-standing GMS-sheet with hierarchical pores shows an ultra-high energy density of 793 Wh kg-1 and excellent cycling stability (> 260 cycles) at a practically high current density of 0.4 mA cm-2.

研究分野： エネルギー関連化学

キーワード： Topological Defect　Carbon Materials　Graphene Mesosponge　Lithium-Oxygen Battery

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

Global warming caused by the emission of greenhouse gases has become one of the thorniest problems threatening the survival of mankind. New energy conversion/storage devices are urgently needed to reduce fossil fuel’s depletion. Nonaqueous lithium-oxygen batteries with high theoretical energy density and high discharge potential are becoming an attractive candidate for next-generation energy devices. (Energy Environ. Sci., ***2019***, 12, 887-922.) A typical nonaqueous Li-O_2 battery consists of a Li metal anode, an organic electrolyte, and a gas-breathing porous carbon cathode. Edge sites in conventional carbon are believed to redistribute the local electron density and increase catalytic activity. (Adv. Mater., ***2016***, 28, 6845-6851.) In addition, intrinsic topological defects of carbon materials, such as pentagonal and heptagonal carbon rings, lead to local rehybridization of π-orbitals and create potentially active sites that are beneficial for ORR in the aqueous system. (ACS Nano, ***2011***, 5, 26-41.) However, in a nonaqueous Li-O_2 batteries operating at high voltage, edge sites inevitably lead to severe carbon corrosion. (J. Am. Chem. Soc., ***2013***, 135, 494-500.) Therefore, to reduce the discharge-charge overpotential, non-corrosive carbon materials with many catalytic sites but few edge sites are urgently needed to catalyze the formation and decomposition of insulated discharge products in nonaqueous Li-O_2 batteries. Prior to this research, no one has attempted to use only topological defects without edge sites as active sites in Li-O_2 batteries.

２．研究の目的

The proposed research aims to explore the catalysis of topological defects in Li-O_2 batteries and to improve battery performance by using a corrosion-free carbon cathode with topological defects.

３．研究の方法

This research was conducted under the following five aspects: Material synthesis, topological defect characterization, electrocatalytic mechanism, theoretical calculation, and electrochemical performance.

In FY 2022, I focused on the synthesis of GMS and the characterization of topological defects. In terms of material synthesis, chemical vapor deposition (CVD) and high-temperature treatment (1800℃) were used to synthesize 3-D single-layer GMS using Al_2O_3

nanoparticles as a hard template. (Adv. Funct. Mater., *2016*, 26, 6418-6427.) In addition, free-standing GMS-sheet were also synthesized by CVD. For defect characterization, advanced temperature-programmed desorption (TPD) at up to 1800 ℃ was used to quantify the edge-sites in GMS. N_2 adsorption/desorption tests were used to determine the BET (Brunauer-Emmett-Teller) surface area of GMS. The intensity ratios of the D-band and G-band in Raman spectra were used to quantify the defect of carbons. Atomic-resolution transmission electron microscopy (TEM) and Scanning Electron Microscope (SEM) were also used to identify the microscopy of topological defects in GMS.

In FY2023, I focused on the catalysis of topological defects and the impact on Li-O_2 battery performance. Experimental in-situ and quantitative characterizations as well as theoretical calculations were performed to investigate the catalysis of topological defects. Differential electrochemical mass spectrometry (DEMS) provides real-time information on gas consumption and generation during the discharge-charge process. Density functional theory (DFT) help to understand the reaction processes at the topological defects. Finally, the performance of Li-O_2 batteries based on GMS, GMS-Ru, and optimized free-standing GMS-sheet cathodes was tested with our home-made device to investigate the influence of topological defects on the performance of Li-O_2 batteries.

４．研究成果

In FY 2022, GMS was synthesized by CVD at using a CH_4 as carbon source and spherical Al_2O_3 nanoparticles as hard template (Adv. Sci., *2023*, 10, 2300268.). Advanced TPD was used to precisely quantify the amount of H and O edge sites that are desorbed as H_2, CO, CO_2, and H_2O gases as the sample is heated to 1800 ℃ (inset of Figure 1a). The GMS treated at 1800 ℃ showed only traces of gas evolution, 0.09 mmol g^{-1}, which was the lowest value among the reference carbon materials (Figure 1a), indicating the edge-site-free property of GMS. As shown in Figure 1b, the intensity ratio of the D and G bands (ID/IG ratio) of GMS is 1.45, which is higher than that of the reference carbon (0.87-1.30). This result demonstrates the topological-defect-rich property of GMS, which is supported by the observation of 5,7-membered rings by TEM (Figure 1c). Edge-site-free and topological-defect-rich GMS is promising as a carbon cathode in Li-O2 batteries. In addition, GMS with Ru nanoparticles as solid catalysts, GMS-Ru, were synthesized by chemical refluxing. Free-standing GMS-sheets without binders were also synthesized using Al2O3-sheets as templates. The textural properties of GMS-Ru and GMS-sheets were systematically characterized.

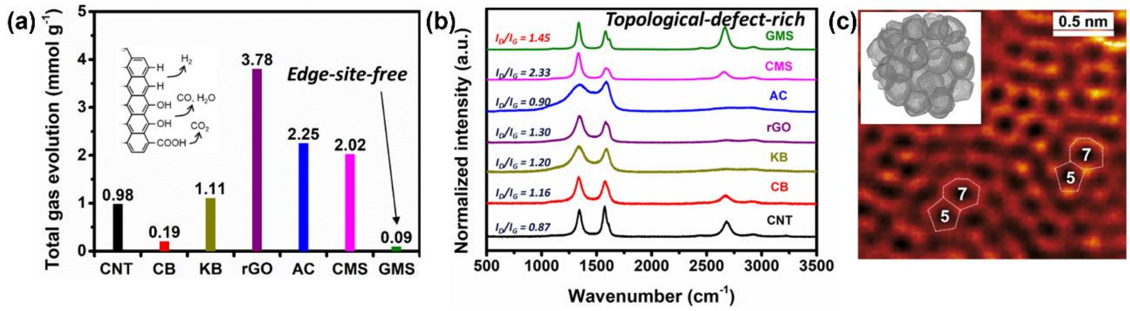

Figure 1 Characterizations of GMS and reference carbons. (a) TPD, (b) Raman spectra, and (c) TEM image of GMS.

In FY 2023, galvanostatic discharge-charge tests were performed with a limited capacity of 0.25 mAh and a current of 0.1 mA to evaluate the cycle stability of the carbon cathodes. The edge-site-free and topological-defect-rich GMS-CP cathode exhibited the longest cycle life. The cycle numbers of the Li-O2 batteries are plotted against TPD total gas evolution and S_{BET}, as shown in Figure 2a. This implies that GMS is a unique and promising carbon cathode for use in Li-O_2 batteries, showing superior stability due to its edge-site-free property and good catalytic performance due to its topological-defect-rich nature. Based on our DFT calculation, the adsorption affinity of LiO_2 for topological defects was stronger than that on the hexagonal rings. Owing to the different adsorption affinity of LiO_2 on hexagonal rings and topological defects, two different Li_2O_2 formation mechanisms occur in GMS-based Li-O_2 batteries, leading to the formation of typical Li_2O_2 toroids and easily-decomposable Li2O2 nanosheets (Figure 2b). Moreover, when we used GMS as a carbon substrate for Ru loading (J. Phys. Chem. C ***2023***, 127, 6239-6247), GMS-Ru exhibited unique sequential catalysis with a low charge plateau owing to topological defect and a reduced second charge plateau owing to Ru catalyst. In our recent work (Adv. Energy Mater. ***2024***, 14, 2303055), free-standing GMS-sheet shows an optimal energy density of 793 Wh kg^{-1} and long-cycle stability (> 260 cycles) at a current density of 0.4 mA cm^{-2}. All the above results prove that GMS with topological defects is one of the best carbon cathodes for Li-O_2 batteries.

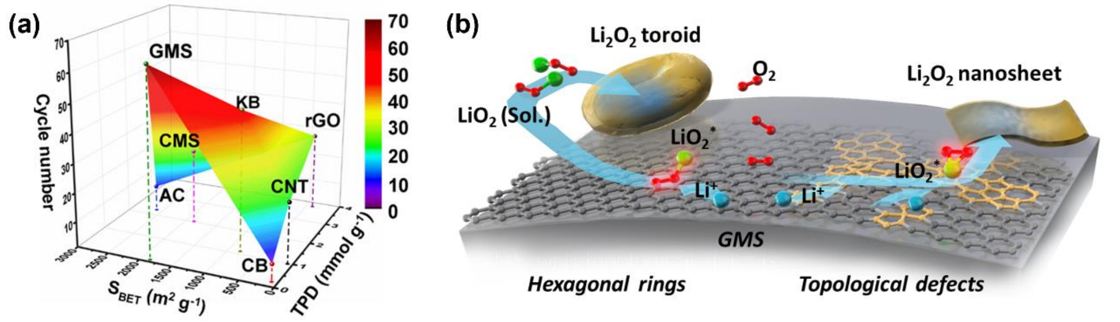

Figure 2 (a) Relationship between the physicochemical properties of carbon materials and the cycle performance of Li-O_2 batteries, (b) Schematic illustrations of discharge mechanism for GMS cathodes.

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　3件）

１．著者名 Yu Wei、Shen Zhaohan、Yoshii Takeharu、Iwamura Shinichiroh、Ono Manai、Matsuda Shoichi、Aoki Makoto、Kondo Toshihiro、Mukai Shin R.、Nakanishi Shuji、Nishihara Hirotomo	４．巻 14
２．論文標題 Hierarchically Porous and Minimally Stacked Graphene Cathodes for High‐Performance Lithium?Oxygen Batteries	５．発行年 2024年
３．雑誌名 Advanced Energy Materials	６．最初と最後の頁 2303055
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/aenm.202303055	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

１．著者名 Tang Rui、Aziz Alex、Yu Wei、Pan Zheng‐Ze、Nishikawa Ginga、Yoshii Takeharu、Nomura Keita、Taylor Erin E.、Stadie Nicholas P.、Inoue Kazutoshi、Kotani Motoko、Kyotani Takashi、Nishihara Hirotomo	４．巻 -
２．論文標題 Prominent Structural Dependence of Quantum Capacitance Unraveled by Nitrogen‐Doped Graphene Mesosponge	５．発行年 2023年
３．雑誌名 Small	６．最初と最後の頁 2308066
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/smll.202308066	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

１．著者名 Liu Hongyu、Shen Zhaohan、Pan Zheng-Ze、Yu Wei、Nishihara Hirotomo	４．巻 15
２．論文標題 Cathode Chemistries of Lithium-Oxygen Batteries in Nanoconfined Space	５．発行年 2023年
３．雑誌名 ACS Applied Materials & Interfaces	６．最初と最後の頁 40397～40408
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsami.3c05944	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 該当する

１．著者名 Shen Zhaohan、Yu Wei、Aziz Alex、Chida Koki、Yoshii Takeharu、Nishihara Hirotomo	４．巻 127
２．論文標題 Sequential Catalysis of Defected-Carbon and Solid Catalyst in Li?O₂ Batteries	５．発行年 2023年
３．雑誌名 The Journal of Physical Chemistry C	６．最初と最後の頁 6239～6247
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.jpcc.3c01042	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 該当する

1．著者名 Yu Wei、Yoshii Takeharu、Aziz Alex、Tang Rui、Pan Zheng‐Ze、Inoue Kazutoshi、Kotani Motoko、Tanaka Hideki、Scholtzov? Eva、Tunega Daniel、Nishina Yuta、Nishioka Kiho、Nakanishi Shuji、Zhou Yi、Terasaki Osamu、Nishihara Hirotomo	4．巻 10
2．論文標題 Edge‐Site‐Free and Topological‐Defect‐Rich Carbon Cathode for High‐Performance Lithium‐Oxygen Batteries	5．発行年 2023年
3．雑誌名 Advanced Science	6．最初と最後の頁 2300268
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/advs.202300268	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

〔学会発表〕　計7件（うち招待講演　0件／うち国際学会　4件）

1．発表者名 Wei Yu, Takeharu Yoshii, Shoichi Matsuda, Makoto Aoki, Toshihiro Kondo, Hirotomo Nishihara
2．発表標題 Free-standing hierarchical porous carbon cathode for practical Li-02 batteries
3．学会等名 Carbon2023（国際学会）
4．発表年 2023年

1．発表者名 Wei Yu, Alex Aziz, Takeharu Yoshii, Hirotomo Nishihara
2．発表標題 Insight into carbon edge sites in lithium-oxygen batteries
3．学会等名 Faraday discussion（国際学会）
4．発表年 2023年

1．発表者名 Wei Yu, Alex Aziz, Takeharu Yoshii, Hirotomo Nishihara
2．発表標題 Elucidation of carbon corrosion in lithium-oxygen batteries
3．学会等名 7th CBNM（国際学会）
4．発表年 2023年

１．発表者名
Wei Yu, Takeharu Yoshii, Alex Aziz, Hirotomo Nishihara

２．発表標題
The culprit of carbon corrosion in Li-02 batteries: H-containing edge sites

３．学会等名
第50回炭素材料学会年会

４．発表年
2023年

１．発表者名
Wei Yu, Takeharu Yoshii, Rui Tang, Zheng-Ze Pan, Hirotomo Nishihara

２．発表標題
GO/mesoporous Carbon Composite Membrane for Durable Cathode of Li-02 Batteries

３．学会等名
第17回　酸化グラフェン学会

４．発表年
2022年

１．発表者名
Wei Yu, Takeharu Yoshii, Rui Tang, Zheng-Ze Pan, Hirotomo Nishihara

２．発表標題
Influence of Carbon Cathode Edge Sites on Li-02 Batteries

３．学会等名
The 2022 World Conference on Carbon（国際学会）

４．発表年
2022年

１．発表者名
Wei Yu, Takeharu Yoshii, Alex Aziz, Rui Tang, Zheng-Ze Pan, Hirotomo Nishihara

２．発表標題
In Pursuit of High-Performance Carbon Cathodes for Li-02 Batteries

３．学会等名
第49回炭素材料学会年会

４．発表年
2022年

〔図書〕　計0件

〔出願〕　計2件

産業財産権の名称 リチウム空気電池および多孔質炭素膜の製造方法	発明者 西原洋知、YU WEI	権利者 同左
産業財産権の種類、番号 特許、PCT/JP2022/44070	出願年 2022年	国内・外国の別 外国

産業財産権の名称 リチウム空気電池用正極およびリチウム空気電池	発明者 西原洋知、YU WEI	権利者 同左
産業財産権の種類、番号 特許、PCT/JP2022/026972	出願年 2022年	国内・外国の別 外国

〔取得〕　計0件

〔その他〕

－

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