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研究課題名（和文）Development of photovoltaic redox flow battery using aqueous iodide/triiodide electrolyte

研究課題名（英文）Development of photovoltaic redox flow battery using aqueous iodide/triiodide electrolyte

研究代表者

ＢＹＯＮ　ＨＹＥＲＹＵＮＧ（BYON, HYE RYUNG）

国立研究開発法人理化学研究所・Kim表面界面科学研究室・客員研究員

研究者番号：７０６０６４０９

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研究成果の概要（和文）：リチウムーヨウ素電池(Li-I2 battery)の水溶液上I-/I3-レドックスカップルを光電極(hematite (Fe203)/FTO)接続して、太陽を利用したレドックスフロー電池を作製した。光電極のholeはI-の酸化反応に関与して、その結果、クーロン効率は85%,エネルギー効率は～99.2%に向上させた、30サイクル（～400時間)も安定性能を示した。

研究成果の概要（英文）：The aqueous lithium redox flow batteries are promising in terms of performance, energy density and operation efficiency. Further integrating solar power on this energy system could only be beneficial in both an operational and economical point of view. We demonstrate a novel two-electrode carbon free solar stimulated aqueous Li-I2 battery device, which in situ stores electricity using an aqueous I-/I3- redox couple through the integration of a hematite photoelectrode at the cathode. Under illumination, the electrons and holes stemmed from the absorption of photons are separated in the space charge layer and accumulate within the hematite photoelectrode. The maximum voltage delivered by the cell is more negative under illumination (E-sun = 3.4 V) than in dark (E-dark = 3.55 V) due to this charge injection. The aqueous two-electrode photoassisted battery exhibited robust behavior for 30 cycles (~400 h) with coulombic efficiencies of ~99.2% and energy efficiencies of 85%.

研究分野：　Electrochemistry

キーワード：　Li-I2 battery　photoanode　hematite

１．研究開始当初の背景

(1) Electrochemical rechargeable batteries are currently the most efficient and competent systems for energy conversion and storage (EES), targeted for smart grid (intermittency) and automotive applications. Amongst the various types of these batteries is the aqueous lithium (Li) redox flow battery (RFLB). This energy system combines the alluring features of a redox flow battery (operational flexibility, reliability, long cycle life, power capability and safety) with the large energy density for weight of the Li-ion battery (400 WhL^{-1}) through the introduction of robust redox shuttle molecules for both anode and cathode. [1]

(2) The Li-I_2 battery has been established as a promising energy storage system owing to the high solubility of the I^-/I_3^- redox couple in water ($K_{sp\ KI}$= 8.5 M), the redox potential of the active species ($E^o_{I3-/I-}$ = 0.536 V) since it does not collide with any parasitic reaction(s) such as oxygen evolution ($E^o_{I3-/I-} > E^o_{H2}$), low cost as no organic electrolyte or additive-dye is utilized at the aqueous cathode, robust cyclic performance (η_C =99.5%), long cycle life and high capacity retention (98% of the theoretical capacity ,*viz. 2*11 mAh g^{-1}). [2-3]

(3) A rather novel and prolific area of application for RFLB's is solar energy. Bearing in mind that solar panels are more economical and proficient in generating more power, solar energy has been transformed to a commercially viable source of electricity. Of late, several photorechargeable energy systems have been reported, primarily based on coalescing flow cell technology with well-established dye sensitized solar systems through the incorporation of soluble couples exhibiting facile kinetics bound to in situ convert solar energy to electricity and chemical energy. [3-6]

２．研究の目的

(1) Incorporating in situ solar power on EES systems aspires to create reliable and low-cost systems to target the ever growing energy consumption and demand along with the intermittent nature of solar irradiation. Semiconductor materials comprised of earth abundant materials are optimal inexpensive contenders. Hematite, a n-type semiconductor material is widely used in solar energy conversion technologies due to its auspicious features including a) small bandgap with a potential to convert 16.8% of sun's energy b) chemical stability c) low cost d) abundance e) ease of fabrication and f) environmentally inertness.

(2) By incorporating hematite into the Li-I_2 flow battery we aim to i) reduce the operating cost of the battery (electrode materials contribute up to 30% of the total cost of the battery) and ii) utilize the abundant solar energy to in situ stores electricity using the aqueous I^-/I_3^- redox couple. (Fig. 1a)

３．研究の方法

(1) Formation of hematite films (ϕ=90 nm) from a slightly acidic solution of iron (II) chloride involves the anodic electrodeposition of ferric oxy-hydroxide followed by annealing oxidation in air at 823 K for 50 minutes to induce the activation of pure hematite (Fig. 1b). The structure of the two-electrode aqueous Li-I_2 battery was as follows: FTO-hematite cathode|cylindrical glass-shell|LATP|cylindrical glass-cell, sealed all together in sequence. The preparation of the anode compartment was conducted in an argon-filled glove box where a thin and flat Li metal was attached to a copper mesh on the second cylindrical glass shell. A polymer buffer layer was put between the Li metal and separator (LATP) to impede the formation of dendritic Li. The non-aqueous electrolyte of 1 M LiTFSI in EC/DMC was used as the anode electrolyte. The final step of the assembly involved the injection of the aqueous electrolyte (2 M KI, 0.2 M I_2) with a total volume between 140 and 170 µl.

４．研究成果

(1) A ground two-electrode carbon-free solar stimulated aqueous Li-I_2 battery device, which in situ stores electricity using an aqueous I^-/I_3^- redox couple through the integration of a hematite photoelectrode at the cathode is being demonstrated. Exposure to visible light drives the separate redox couples (I^-/I_3^- and Li/Li^+) and a current through the external load.

(2) The photoassisted charging process has been constructive for the two-electrode aqueous battery since the solar energy captured can be pumped from the energy level of the I^-/I_3^- redox couple to the energy level of the conduction band

of hematite leading to i) a reduction in the charging and consecutively the overall cell voltage and ii) a boost in the voltage and energy efficiencies (Fig. 1c).

(3) The aqueous two-electrode photoassisted battery exhibited robust behavior for 30 cycles with coulombic efficiencies of ~99.2% and energy efficiencies of 85%. No capacity fading was apparent for ~400 h of continuous cycling (Q = 177 mAh.g^{-1} at a current rate of 0.3 mA.cm^{-2}) while a gravimetric energy density of 0.6 Wh.kg^{-1} was achieved analogous to other EES systems. Hematite exhibited good stability under 400 h of continuous operation preserving its photoactivity while no noticeable change on the performance of the separator (LATP) was witnessed.

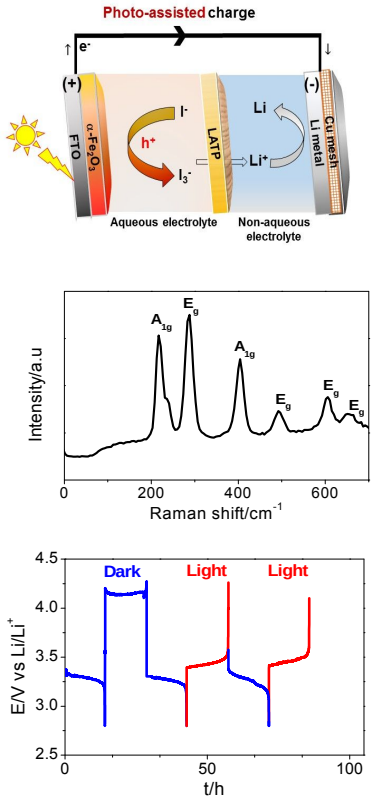

Figure 1. a) Schematic of the two-electrode aqueous Li-I_2 battery with a hematite photoelectrode as positive electrode. b) Raman spectra of the hematite film. Inset shows digital picture of the hematite|FTO photoelectrode. c) Cyclic performance, first cycle under dark ($E_{charging}$=4.15 V), second and third cycles on light response ($E_{charging}$=3.42 V) at a current density of 0.075 mA cm^{-2}.

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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　1　件）

High energy efficiency and stability for photo-assisted aqueous lithium-iodine redox batteries
Nikiforidis, G.; Tajima, K.; Byon, H. R*
***ACS Energy Lett.* 2016,** *1,* 806-813.

〔学会発表〕（計　2　件）

(1) 11/2015: Nikiforidis, G.; Byon, H. R, 56th Battery Symposium in Japan, Nagoya, “Solar-stimulated aqueous Li-I_2 Battery”

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〔図書〕（計　0　件）

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権利者：
種類：
番号：
出願年月日：

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発明者：
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種類：
番号：
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国内外の別：

〔その他〕
ホームページ等
http://www.riken.jp/byoniru/

６．研究組織
(1)研究代表者
卞 惠鈴（BYON, Hye Ryung ）
理化学研究所，
Kim 表面界面科学研究室，客員研究員
研究者番号：70606409

(2)研究分担者
（　　）

研究者番号：

(3)連携研究者
（　　）

研究者番号：