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Short Communication

An Approach to Solar Rechargeable Flow Battery Based on Electroactive Organic Redox Couples

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An integrated photo-electrochemical solar energy conversion and storage device is developed by a dye sensitized TiO_2 solar cells and 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO) / 1, 4-Benzoquinone (BQ) redox flow batteries. The device can be directly charged by solar light without external bias, and discharged like normal RFBs with an energy storage density of 3.5 $mAhg^{-1}$ over many cycles. The proposed device demonstrates a rapid photo-charge at light illumination and a stable electrochemical discharge in the dark, realizing an in situ photo-to-chemical-to-electrical conversion and photo-to-chemical storage.

Keywords: Solar cells; Rechargeable flow battery; Charge storage; Organic redox couples

1. INTRODUCTION

Seeking for sustainable energy is one of the most significant challenges in our modern society. The use of fossil energy resources has produced massive amount of pollution, destroys climate and reduces the natural resources in the earth. Thus, it is necessary to explore alternative clean and renewable energy sources, among which solar energy is recognized to be an ideal choice for the future[1]. In the past decades, dye-sensitized solar cells (DSSC) have developed into a hopeful devices for low-cost, large-scale solar energy transformation, because of their advantages of efficiency, price and technological simplicity compared with silicon–based photovoltaic cells[2]. However, they are not suitable for electric storage. We know that solar energy is hardly to store due to its dispersity and intermittency, which limits its application in our daily life. Thus, Innovative solar storage technologies are urgently needed to meet the fast-growing demand for solar energy usage.

In recent years, It is conventional to combine dye-sensitized solar cell (DSSC) with external rechargeable batteries for the in situ conversion of solar energy to electricity and chemical energy, which were known as photovoltaic self-charging batteries (as PV-battery). Sunlight, an abundant clean source of energy, can alleviate the energy limits of batteries, while batteries can address photovoltaic intermittency[3-5]. In the system, a third accessorial electrode was introduced in a DSSC for photogenerated charges storage, such as WO_3 and polypyrrole[6-10]. Nevertheless, all the above batteries have their boundedness owing to the fixed model and limited capacity of solid material, because of the electrical storage capacity of photorechargeable batteries is proportional to the size of DSSC and quality of electroactive material[11]. PV-battery system design have became one of the greatest challeges towards improving storage capacity and large-scale implementation of this technology. An organic-inorganic hybrid photoelectrochemical storage cell (PESC) have been develepted to capture and store energy[9,12]. In addition, consisting of dye-sensitized solar cells and electrochemical cells is used for hydrogen production and storage[13].

It should be noted that the redox-flow batteries (RFBs) utilize two soluble redox couples and have lots of advantages, such as convenient design, low-cost and long lifetimes, which are considered as an attractive approach for the storage of large-scale electrical energy[14-17]. With this in mind, we try to separate the photo anode and cathode by a lisicon film, and then two kinds of liquid active electrolytes are injected into the chamber respectively. For further investgation, one pump is placed between the can of raw electrolyte and charging chamber, while another pump is placed between the charging chamber and the product electrolyte to realize the circulation. Then a light-rechargeable redox-flow battery(LR-RFB) based on dye-sensitized solar cell is fabricated.

In this communication, we involve an original LR-RFB device which is developed by integrating a dye sensitized TiO_2 solar cells with 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO) / 1, 4-Benzoquinone (BQ) RFBs. The proposed device demonstrates new solar cell systems in order to convert and store solar energy.

2. EXPERIMENTAL

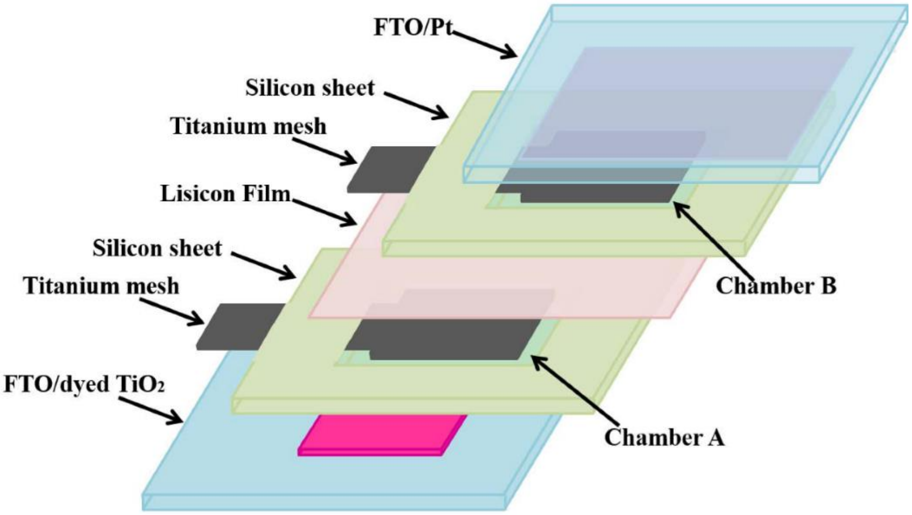

Figure 1. Cell construction of the light-rechargeable redox-flow battery

A regular TiO_2 photo-anode of dye-sensitized solar cell (DSSC) was made by doctor-bladed method, sintered at 500 ℃ and then immersed in D102 dye solution for 12 hours. The TiO_2 paste was made by ball milling of the mixture contains 0.6 g P25 (20 nm TiO_2, Degussa), 0.12 g ethyl cellulose, 1 mL terpineol and 9 mL ethanol absolute. The counter electrode of Platinum coated on fluorine-doped tin oxide conductive glass (15 Ω/cm^2, Nippon Sheet Glass, FTO) was prepared by electrochemical deposition in a solution containing 0.05 mM chloroplatinic acid in H_2O. The electrochemical deposition lasted for 120 minutes at the potential of 2.0 V in a two electrodes system with a Pt foil counter electrode.

The cell construction of the LR-RFB system is shown in 0. The system consists of dyed TiO_2 on FTO, titanium mesh with silicon sheet, Lisicon film, another titanium mesh with silicon sheet, and Pt deposited FTO from bottom to up. Then, the five parts are pressed tightly and clipped together. The vacant space in the silicon sheet forms chamber A and chamber B respectively. Chamber A is injected with anode electrolyte (0.1 M TEMPO and 0.2 M $LiClO_4$ in Propylene carbonate(PC)), while Chamber B is injected with cathode electrolyte (0.1M 1,4-Benzoquinone(BQ) and 0.2 M $LiClO_4$ in PC). Then, a simple LR-RFB is accomplished. And the integrate structure reveals as FTO / dyed TiO_2 / 0.1 M TEMPO and 0.2 M $LiClO_4$ in PC (Chamber A) / Lisicon film / 0.1M 1,4-Benzoquinone (BQ) and 0.2 M $LiClO_4$ in PC (Chamber B) / Pt / FTO. And the chamber A and chamber B are connect with the outside plant by titanium meshes.

In order to confirm the electric potential of the active materials, cyclic voltammetry (CV) method is involved by CHI600A electrochemical workstation (Shanghai, China). And the voltage change of the LR-RFB were recorded with an IM6e (Zahner) electrochemical workstation. The light source for the photocharge was a solar light simulator (300W, Orial , Hongkong Keyi) with a power density of 100 $mW{\bullet}cm^{-2}$.

3. RESULTS AND DISCUSSION

The working mechanism of the integrated LR-RFB is illustrated in 0. The whole system is separated by the lisicon film into two parts with parallel structures. The active electrolyte is stored in the electrolyte tank, promoted by the pump, and reacted in the chamber of each side. The reactions in the system comprise photo-charge process indicated by the green arrows and electrochemical discharge process indicated by the black arrows. When the cell is photocharged, the photo-anode (A) and the counter cathode electrode (B) are connected by copper wires while the anode (C) and cathode (D) are open circuited. The dye molecules on photo anode are exicited and split into electrons and dye cation (D^+) with illumination. The photo-generated electrons arrived at the counter electrode (B) through the external circuit where the BQ is reduce to BQ^-, while the strong oxidizing D^+ oxidize the TEMPO into $TEMPO^+$. In the meantime, Li^+ ions migrate from chamber A to chamber B to achieve the cycle and keep ions equilibrium. During the electrochemical discharge process, anode collector (C) and cathode collector (D) are connected while the photo-anode (A) and the counter cathode electrode (B) are disconnected in a blackbox. Since the balance potential of $TEMPO^+/TEMPO$ is higher than that of BQ/BQ^-, electrons can pass from BQ^- anions to $TEMPO^+$ cations through the collectors and external circuit. As BQ^- anions and $TEMPO^+$ cations come back to TEMPO and BQ, Li^+ ions migrate from chamber B back to chamber A accordingly to accomplish the discharge process.

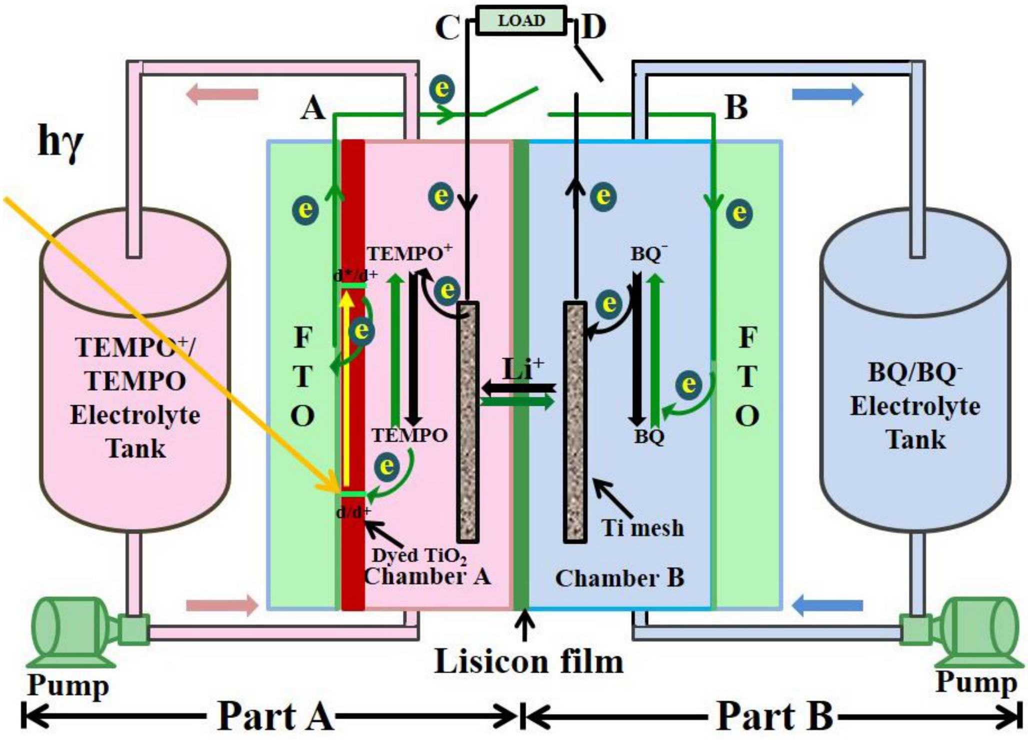

Figure 2. Schematic demonstration of the working mechanism of the LR-RFB.

(A lisicon film is used as the seperator and two pieces of titannium meshes are used as the current collectors.)

The photo-charge and electrochemical-discharge process of the LR-RFB showed as below:

Photo-charge process:

Reaction in chamber A (A electrode):

$$\mathrm{Dye} \xrightarrow{h\gamma} \mathrm{Dye}^{*}(\mathrm{Dye}^{+} + \mathrm{e}^{-}) \qquad (1)$$

$$\mathrm{TEMPO} + \mathrm{Dye}^{+} \rightarrow \mathrm{TEMPO}^{+} + \mathrm{Dye} \qquad (2)$$

Reaction in chamber B (B electrode):

$$\mathrm{BQ} + \mathrm{e}^{-} \rightarrow \mathrm{BQ}^{-} \qquad (3)$$

Thus, the overall reaction of photo-charge process:

$$\mathrm{TEMPO} + \mathrm{BQ} \xrightarrow{h\gamma} \mathrm{TEMPO}^{+} + \mathrm{BQ}^{-} \qquad (4)$$

Electrochemical discharge process:

Reaction in chamber A (C electrode):

$$\mathrm{TEMPO}^{+} + \mathrm{e}^{-} \rightarrow \mathrm{TEMPO} \qquad (5)$$

Reaction in chamber B (D electrode):

$$\mathrm{BQ}^{-} \rightarrow \mathrm{BQ} + \mathrm{e}^{-} \qquad (6)$$

Overall reaction of electrochemical discharge process:

$$\mathrm{TEMPO}^{+} + \mathrm{BQ}^{-} \rightarrow \mathrm{TEMPO} + \mathrm{BQ} \qquad (7)$$

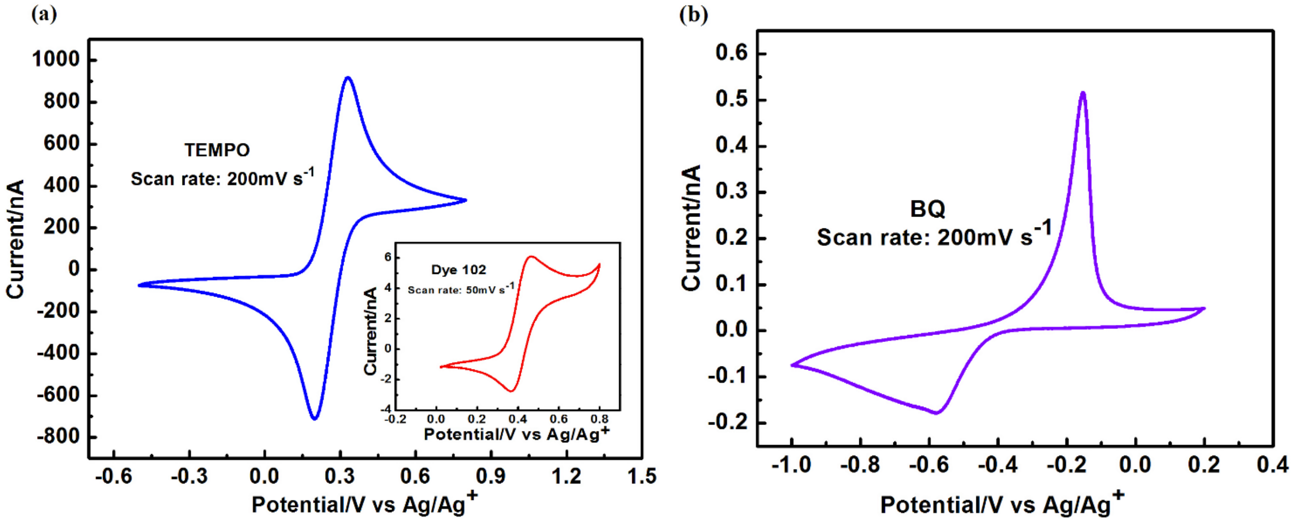

Figure 3. Cyclic voltammograms of (a) TEMPO&D102 and (b) BQ on Pt disc (100 μm diameter) in 1.0M $LiClO_4$/PC solution

Theoretically, the feasiblity of the LR-RFB system depends on two aspects, the potential difference between the D102 and TEMPO as well as the potential difference between BQ and conduction band of TiO_2. And the LR-RFB system open-circuit voltage relies on the discrepancy of the balance potential between $TEMPO^+$/TEMPO and BQ/BQ^-. 0 lists the cycle voltammetrys (CVs) of TEMPO, dye D102 and BQ. As revealed in 0a, the TEMPO electrolyte shows a pair of terrific reversible redox peaks between +0.2 V and +0.33 V vs Ag/Ag^+ reference electrode, while the D102 gives a pair of reversible redox peaks between +0.37 V and +0.46 V vs Ag/Ag^+. The oxidation potential peak of the dye (+0.46 V) is extremely higher than the reduction potential of TEMPO (+0.2 V), which indicates that TEMPO can be easily oxidized by D102 into $TEMPO^+$ at the photo-anode during photo-charging. 0b shows the CV curve of BQ/BQ^- redox couple, with the reduction peak and oxidation peak appears at −0.58 V and −0.16 V, respectively. In aprotic solvents, the potential of the TiO_2 conduction band edge is about −0.68 V vs Ag/Ag^+[18] , which is much lower than the reduction potential of the BQ (−0.58 V). It means that the BQ can be easily reduced to BQ^- at the counter electrode. Thus, the whole process is completely doable. Compared with open-circuit potential of 0.6 V between DMFc+/DMFc and I^{3-}/I^- [13], the current couples shows higher open-circuit potential at 0.7 V, while as the balance potential of $TEMPO^+$/TEMPO and BQ/BQ^- are +0.27 V and –0.43 V respectively.

In order to evaluate the LR-RFB system, the LR-RFB is photo-charged by short-circuited the photo-anode (A) and the counter cathode electrode (B) in illumination, while a voltmeter is imposed between anode collector (C) and cathode collector (D). And electrochemical discharge happens when C and D are connected to allowed a constant current of 50 μA/cm^2 to flow through while A and B are disconnected. 0a shows the voltage change between C and D during the photo-charge process and the electrochemical discharge process. It is obviously that the voltage rises rapidly to about 0.66 V as soon as the photo-anode exposed to light, which indicates the establishment of the voltage between $TEMPO^+$/TEMPO and BQ/BQ^- redox couples. As the accumulation of $TEMPO^+$ and BQ^- through continued illumination, the voltage rises slowly, which can be explained by the Nernst equation. When the photo-charge process finished, the LR-RFB discharge with a platform at about 0.5 V in the dark, which testify the reaction happens between the two redox couples. The discharge platform is 0.2V higher than that of DMFc+/DMFc and I^{3-}/I^- couples[13], which indicate lower polarization. In an other hand, the platform starts at about 0.58 V, which is consistent with the potential difference between the start potential of the oxidizion of BQ^- (−0.3 V) and start potential of the reduction of $TEMPO^+$ (+0.3 V). So we can confirm that the LR-RFB is feasible to be an in situ light rechargeable and energy storable system. As shown in 0b, the overall discharge capacity of TEMPO and BQ is about 3.5 $mAhg^{-1}$,which is lower than that of the capacity of 8.3 $mAhg^{-1}$ with static structure[8]. Considering the discharge platform voltage of 0.5V, the energy density in this work is 1.75 $mWhg^{-1}$, while the energy density is calculated as 3.32 $mWhg^{-1}$ with static structure[8], which shows better energy performance.

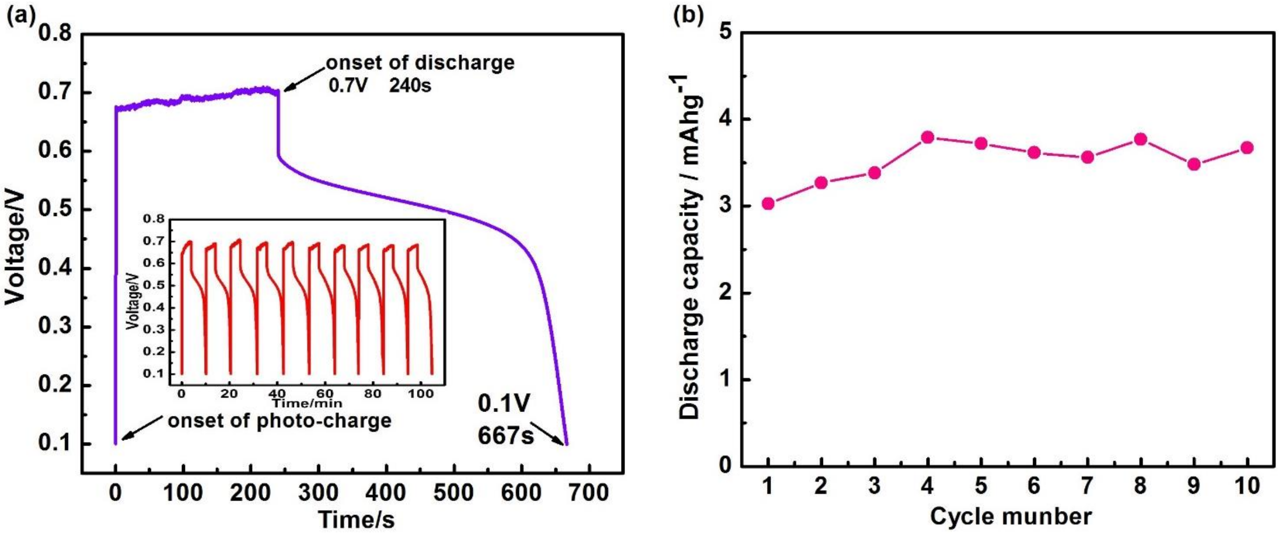

Figure 4. (a) Voltage change of the LR-RFB when photo-charge under irradiation and electrochemical discharge at 50 μA/cm^2. (b) diacharge capacity for the first ten cycles.

4. CONCLUSIONS

In conclusion, we propose a new type of LR-RFB based on DSSC and redox-active $TEMPO^+/TEMPO$ and BQ/BQ^- couples. It is demonstrated that the LR-RFB fabrication can provide an integrate solar-to-chemical energy conversion and storage device. And as shown in this communication, the solar-electrochemical performance of the LR-RFB system largely depends on the properties of the energy storable materials, such as balance potential, concentration, redox reversibility and so on. Thus, to find proper energy storable materials for LR-RFB may promote further applications of solar energy utilization.

ACKNOWLEDGEMENTS
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