Highly efficient harvesting and storage of solar energy by photoelectrocatalytic conversion of fast kinetics redox couples on dual-silicon electrodes

Jingying Shi,[a,*] **Shicao Liao**,[a,b] **Can Li**[a,*]
[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences; Dalian National Laboratory for Clean Energy, Dalian, 116023, China*
[b]*A University of Chinese Academy of Sciences, Beijing, 100049, China*
**Corresponding authors: jingyingshi@dicp.ac.cn; canli@dicp.ac.cn*

Abstract: Taking the advantages of the fast kinetics of quinone/bromine redox couples and wide visible light absorption of silicon photoelectrodes, we designed a dual-silicon photoelectrochemical cell to efficiently convert and store the solar energy in chemicals. Thereafter, a highly efficient solar rechargeable flow cell (SRFC) was fabricated by integrating it with a quinone/bromine RFB for in-situ solar energy harvesting, storage and electricity production.

Keywords: Phototoelectrochemical, redox couples, storage of solar energy.

1. Introduction

Although directly storing solar energy in H_2 produced by light-driven water splitting has been regarded as the most attractive way, challenges with hydrogen storage and the expense of fuel cells impede the wide implementation of solar-hydrogen/fuel cell hybrid systems. Moreover, the sluggish half reaction kinetics of water oxidation greatly restricts the improvement of solar energy conversion efficiency in water splitting as indicated in our previous reports.[1, 2] Alternatively, solar energy can also be *in-situ* stored in other chemicals by driving non-spontaneous reactions in photoelectrochemical (PEC) cell.[3] The resulted products can be readily utilized to generate electricity via the reversible chemical reactions. Based on this principle, we designed and fabricated a novel solar rechargeable flow cell (SRFC) by integrating a dual-silicon PEC cell in a quinone/bromine RFB for *in-situ* solar energy conversion and storage.

2. Experimental

Commercial p-Si and n-Si wafers with surface pn junction were used as photocathode and photoanode, respectively. An aqueous solution containing 0.05 M AQDS and1.0 M $H_2SO_4$was used as the catholyte, and an aqueous solution containing 0.2 M HBr and1.0 M H_2SO_4 was used as the anolyte. The solar simulator (AM 1.5G) was used as the light source.

3. Results and discussion

Fig. 1 illustrates the configuration of the SRFC in this work. It consists of a PEC (or photoelectrolysis) cell that deposits solar irradiation into chemical energy and a RFB that converts the as-stored chemical energy into electricity. AQDS/$AQDSH_2$ and Br_3^-/$Br^-$are used as active redox couples. The PEC cell and RFB are connected through electrolyte circuit loops. During the photocharge process, AQDS is reduced to $AQDSH_2$ on the photocathode and Br^- is oxidized to Br_3^-on the photoanode simultaneously in the PEC cell by short-circuiting the two photoelectrodes under illumination. The resultant $AQDSH_2$ and Br_3^- are then stored in two individual reservoirs that can be readily used by the RFB. A commercial Nafion membrane is used to separate the two compartments in each cell.

Reduction and oxidation half reactions during photocharging process are investigated independently. The n^+p-Si coated orderly with metal titanium and TiO_2 thin films as a protective layer (hereafter TiO_2/Ti/n^+p-Si) is employed as the photocathode. Carbon thin film is deposited on its surface as cocatalyst to facile the interfacial electron transfer.The maximum solar-to-$AQDSH_2$ conversion efficiency is calculated to be ca. 6.0 % at the bias of 0.30 V vs. SCE. The p^+n-Si coated with platinum islands as cocatalyst (hereafter Pt/p^+n-Si) is employed as the photoanode. The optimal half-cell solar-to-Br_3^-conversion efficiency is about 11.6% at 0.46 V vs. SCE, which is nearly two times as large as that of solar-to-$AQDSH_2$.

To evaluate the performance of the integrated photoanode/cathode PEC cell, the individual *I-E* data for each photoelectrode is overlaid as shown in Fig. 2. It is seen that the intersection locates at 13.5 mA cm^{-2} at 0.35 V vs. SCE and thus the overall STC ($\eta_{O\text{-}STC}$) is estimated to be 5.9% for the proposed dual-silicon PEC cell, which is much higher than those for direct solar water splitting as well as all the reported SRFCs. Considering that the energy conversion efficiency in this quinone/bromine flow battery is *ca.* 70%, the overall energy conversion efficiency of the present SRFC is estimated to be 4.1% ($\eta_{overall} = \eta_{O\text{-}STC} \times \eta_{RFB}$ = 5.9% × 70%). It should be pointed that no bias is required to drive the overall photocharge reactions. Stability tests illustrate both photoanode and photocathode can sustain for at least 10 h under AM 1.5 G irradiation and 37-100 h under visible light. The photocharge/dark-discharge tests in our proof-of-concept SRFC demonstrate that the cell voltage can be self-charged to 0.8 V under simulated AM1.5 G illumination and the discharge capacity is up to 730 mAh L^{-1} after photocharging for 2 h.

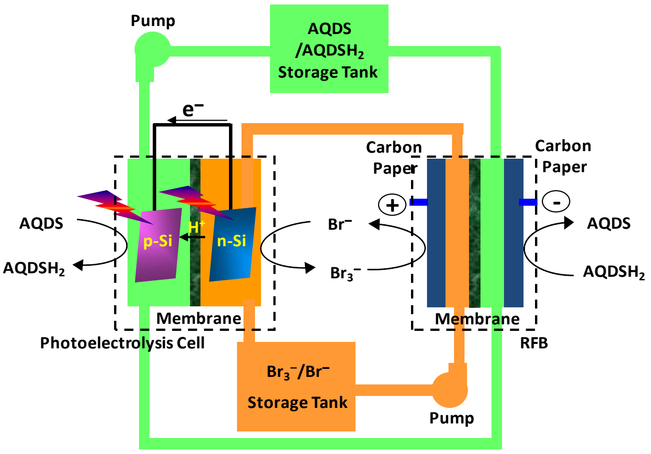

Figure 1. Schematic configuration and working mechanism of the SRFC based on AQDS/$AQDSH_2$ and Br_3^-/Br^- redox couples.

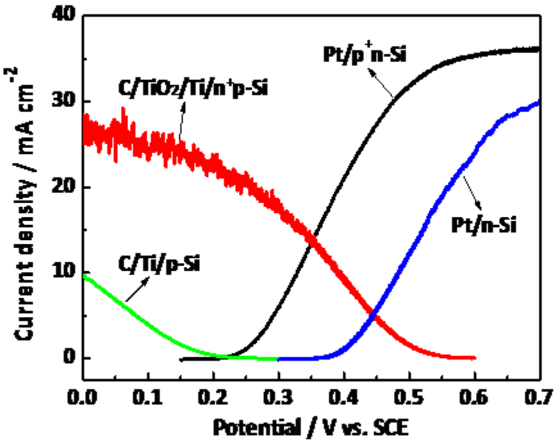

Figure 2. Overlaid current–potential curves of the individually photocathodes and photoanodes.

4. Conclusions

In summary, we designed and fabricated a SRFC device with the dual function of conversion and storage of solar energy via direct integration of a dual-silicon PEC cell and a RFB using water-soluble AQDS/$AQDSH_2$ and Br_3^-/Br^-redox couples as the energy carriers. This is for the first time to demonstrate a promising application of SRFC with outstanding overall energy conversion efficiency, high discharge voltage and desirable discharge capacity based on earth-abundant electrodes and fast aqueous soluble redox couples.[4]

References

1. C. M. Ding, W. Qin, N. Wang, G. J. Liu, Z. L. Wang, P. L. Yan, J. Y. Shi, C. Li, Phys. Chem. Chem. Phys. 16(2014) 15608-15614.
2. G. J. Liu, J. Y. Shi, F. X. Zhang, Z. Chen, J. F. Han, C. M. Ding, S. S. Chen, Z. L. Wang, H. X. Han, C. Li, Angew. Chem. Int. Ed. 53(2014) 7295 -7299.
3. F.-R. F. Fan, H. S. White, B. L.Wheeler, A. J. Bard, J. Am. Chem. Soc.102(1980) 5142-5148.
4. S. C. Liao, X. Zong, B. Seger, T. Pedersen, T. T. Yao, C. M. Ding , J. Y. Shi, J. Chen and C. Li. Nat. Commun. 7(2016): 11474.