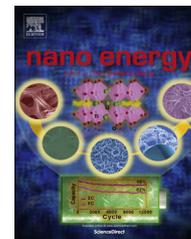


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FULL PAPER

Unbiased solar energy storage: Photoelectrochemical redox flow battery



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Cadmium sulfide

Abstract

Electricity from renewable energy sources is craving for efficient storage technologies, in particular solar industry, to enable practical small-scale solutions for residential and offices use. The best stationary technology is probably the redox flow batteries. This article proposes the direct conversion of sunlight into electrochemical energy stored in a redox flow battery. A photoelectrochemical cell is used to charge a vanadium redox flow cell (CdS(s)|V³⁺, VO²⁺||V³⁺, V²⁺|Carbon Felt(s), E⁰=0.6 V_{NHE}). A CdS thin film photoelectrode is prepared to directly charge the cell, pairs V³⁺/VO²⁺. CdS photoanode exhibits competitive photocurrents, when compared to other photoelectrochemical devices, and yields enough photovoltage to charge the vanadium battery up to 75% with no external bias. An overlayer of CdSe improves the performance of CdS with current densities up to ca. 1.4 mA cm⁻². Finally, a tandem configuration is tested using a dye-sensitized solar cell and a CdS photoanode creating ~1.3 V of photovoltage. This tandem arrangement proves to charge conventional all vanadium redox cell (DSC/CdS(s)|VO²⁺, VO²⁺||V³⁺, V²⁺|Carbon Felt(s), E⁰=1.2 V_{NHE}) without external bias.

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Introduction

The efficient exploitation of renewable energy sources is the only route for long-term energy supply. However,

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renewable energy is often intermittent, local in nature [1] and there is an inherent mismatch between production and consumption. If future goals of fully renewable energy sources are to be met it is paramount that efficient storage technologies are developed. Compared to other storage systems, such as conventional batteries, gravity or mechanical-based and supercapacitors, that can be used for the applications requiring moderate energies and high power densities, chemical fuels combine the advantages of ease of transportation and high-energy storage densities [2-4].

For the past two decades, storage in hydrogen through electrolysis of PV electricity or direct photoelectrochemical water splitting has been some of the most investigated technologies for storage of solar energy [5-8]. Much effort was devoted to fabricate and optimize photoelectrochemical (PEC) cells for water splitting offering the prospect of clean, dispatchable, abundant, and affordable energy. However, hydrogen is a very low-density gas requiring high-end technology for storage and transport. Also, its production via PEC cells route still presents many unsolved challenges, in particular low conversion efficiency [9,10]. PEC cells require an abundant semiconductor material with a band gap energy (E_g) large enough to split water and a conduction band-edge energy (E_{cb}) and valence band-edge energy (E_{vb}) that straddle the electrochemical potentials for generation of hydrogen (E_{H^+/H_2}^0) and oxygen (E_{O_2/H_2O}^0) [9]. This requirement limits the possibilities to a handful of semiconductor materials. Since the positions of both the band edges in many semiconductors and $E_{H^+/H_2}^0/E_{O_2/H_2O}^0$ shift with -59 mV per pH unit [2], pH-tuning strategies to match energy levels are not effective.

In a PEC cell, the photo induced free charge carriers migrate to a semiconductor/liquid junction reacting with electroactive species directly at the semiconductor interface. Given the energy efficiency losses at semiconductor/liquid junctions due to the concentration and kinetic

overpotentials needed to drive the hydrogen and oxygen evolution reactions, the energy required for photoelectrolysis is frequently reported to have values around 2 eV per electron-hole pair generated [2,11]. Considering the significant amount of research in the field for the past two decades, practical semiconductor solutions that enable unbiased and efficient single photoelectrode solar water splitting appear unlikely.

The use of photoelectrodes for converting solar into electrochemical energy in a redox flow battery (RFB) arrangement is a disruptive approach that allows an efficient storage of solar energy. Contrary to water splitting, where oxidation and reduction potentials are unique, in the case of direct solar charging redox flow batteries it is potentially possible to find two redox pairs for a selected photoelectrode, fitting the redox potentials with the semiconductor band edges. Moreover, the round trip energy efficiency using redox pairs for storing electricity is very high, ca. 85%, compared to hydrogen with round trip energy efficiencies of 20-50% [12]. The direct solar charging of redox flow batteries is then viewed as a premium opportunity for the research on photoelectrochemical cells.

Preliminary experiments using a photoelectrode for charging redox pairs have been reported in the 80s but limited choice of redox pairs and membrane limitations made the combined PEC and RFB device unable to efficiently convert solar into electrochemical storable energy and research in this topic came to a halt for decades [13,14]. Compared to PEC water splitting, for solar-RFB there are multiple choices of the redox couples given a great flexibility for choosing suitable photoelectrodes. Semiconductors that are unsuitable for water splitting due to thermodynamic potential mismatch or corrosion may now be used for solar-RFB since the choice of redox pairs is quasi-unlimited with redox potentials varying almost continuously [15-17]. Furthermore, most of the charge transfer processes involving redox couples normally used in RFB have faster kinetics since they

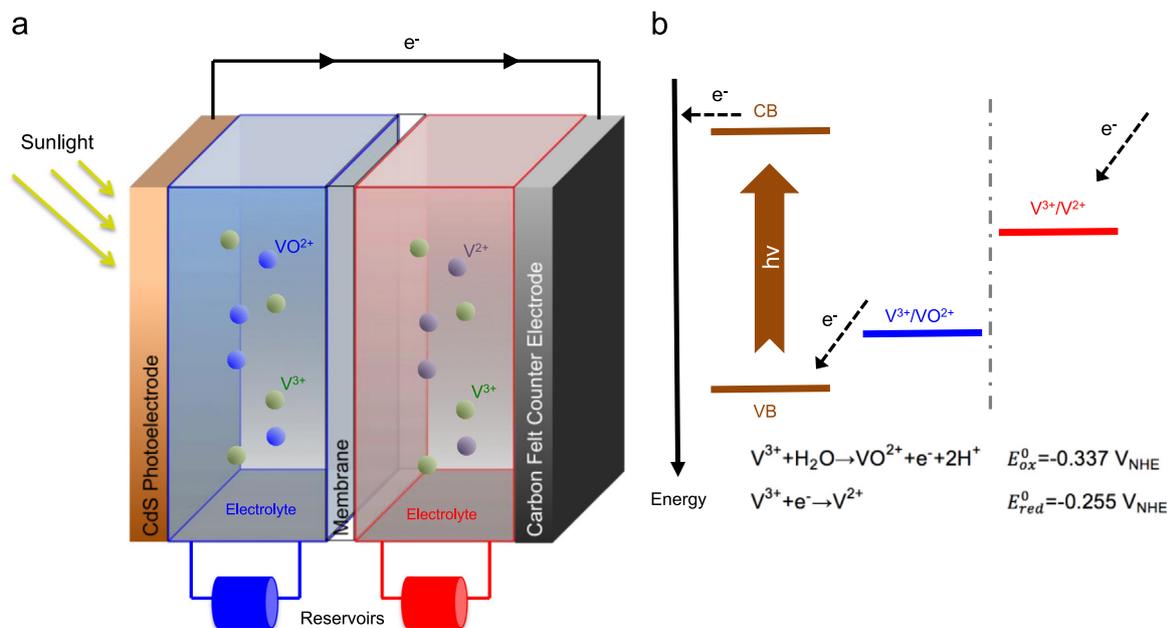


Figure 1 Schematic diagram of (a) all vanadium solar redox flow battery charged with a CdS photoanode and (b) energy diagram of the system, including the standard redox reactions.

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