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Short communication

All-vanadium redox photoelectrochemical cell: An approach to store solar energy

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ABSTRACT

A highly-efficient all-vanadium photoelectrochemical storage cell has been demonstrated in this work. This storage cell takes advantage of fast electrochemical kinetics of vanadium redox couples of VO_2^+/VO^{2+} and V^{3+}/V^{2+}, and appears as a promising alternative to photoproduction of hydrogen from water. Continuous photocharging for 25 h revealed a VO^{2+} conversion rate of 0.0042 μmol/h and Faradaic efficiency of 95% without external voltage bias. The incident photon-to-current efficiency (IPCE) at 350 nm light was calculated to be ~12%.

1. Introduction

Photoproduction of hydrogen from water offers the prospect of using sunlight to produce eco-friendly fuel [1]. While much progress has been made since the pioneering work of Fujishima and Honda more than 40 years ago [1], efficient and cost-effective photoproduction of H_2 still remains unresolved [2]. The highest quantum yield reported is only 5.9% under 420–440 nm light illumination [3], far below the commercializable value of 30% under light of 600 nm [4].

Alternatively, solar energy storage can be realized by photoelectrochemical (PEC) cells [5–7] using photocatalytic reactions of redox species. Utilizing two sets of reversible redox pairs, changes taking place under light illumination can be reversed in the dark when the generated chemical changes drive spontaneous discharge reactions. Previous efforts include employing rechargeable batteries [8,9] in PEC energy storage, integrating a hydrogen bromine-embedded Si system and fuel cell into a regenerative system [5], solid-phase storage couples such as Ag^+/Ag and Cu^{2+}/Cu for a higher capacity, and combining continuous-flow electrolytes of I^{3-}/I^- couples [10] with dye-sensitized solar cells [11]. It has been shown that the PEC storage using redox species can lead to higher levels of photon absorption and more effective charge separation.

In this communication, for the first time, we demonstrated combining PEC energy storage with a vanadium redox-flow battery (VRB), a well commercialized energy storage system for large-scale terrestrial applications. Such an all-vanadium PEC storage cell possesses all merits inherent to VRBs: fast electrochemical kinetics, high charge/discharge round-trip efficiency (up to 90% [12]), low capital cost, and minimal safety issues. Our previous studies [13] have demonstrated facile photooxidation kinetics of VO^{2+} by a wide-band-gap TiO_2 photoanode, presenting the promise of a drastic enhancement in efficiency of the all-vanadium PEC storage cell.

2. Experimental

The schematic of the all-vanadium PEC storage cell is illustrated in Fig. 1. The cell consists a TiO_2 working electrode as the photoanode, a Pt-mesh counter electrode, and two redox couples, i.e., VO_2^+/VO^{2+} and V^{3+}/V^{2+}, separated by a Nafion 117 membrane. 3 M H_2SO_4 was used as the supporting electrolyte throughout the experiments. The photoanode on a fluorine doped tin oxide (FTO) glass was fabricated using a slurry consisting of 0.5 g TiO_2 powders (VP AEROPERL® P 25/20), 0.25 g ethyl cellulose, 0.062 g polyvinylidene fluoride (PVDF), and 2.15 g α Terpineol. After sintering in air the photoelectrode had a thickness of 10 μm and an active area of 6.45 cm^2.

Photoelectrochemical studies were conducted using a potentiostat (Princeton Applied Research, PARSTAT 2273) and a customized two-chamber H-cell. Electrolytes of 0.01 and 0.1 M VO^{2+} were prepared by dissolving $VOSO_4 \cdot xH_2O$ (99.9%, Alfa Aesar) in 3 M H_2SO_4. The V^{3+} solution was prepared from a VO^{2+} electrolyte in an electrochemical cell with static electrolyte under a constant current of 3 mA according to references [14,15]. The light source was an ozone-free solar simulator system (Newport, USA). A 300 W Xe lamp with a series of long-

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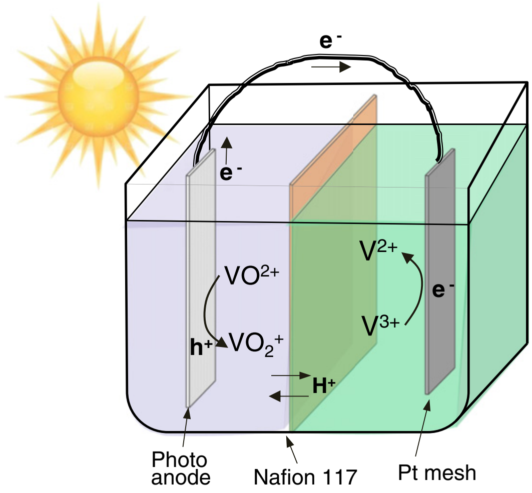

Fig. 1. Schematic illustration of the all-vanadium redox PEC storage cell.

pass filters was used to illuminate the photoelectrode. Small amount of the electrolyte in a quartz cuvette was analyzed using a UV–vis spectrophotometer (PerkinElmer Lambda 35) to determine the electrolyte composition change. For the incident photon-to-current efficiency (IPCE) measurements, the wavelength of the incident light was controlled by a monochromator (Optometrics). The IPCE was calculated according to the following equation:

$$\mathrm{IPCE} = (1240I)/\left(\lambda \cdot J_{\mathrm{light}}\right) \tag{1}$$

where I (A/cm^2) is the measured photocurrent density at a specific wavelength, λ (nm) is the wavelength of incident light, and J_{light} (W/cm^2) is the light irradiance determined by a photodetector (Newport, USA).

3. Results and discussion

Fig. 2 compares the proposed all-vanadium redox PEC storage with photocatalytic water splitting in terms of TiO_2 band positions and the corresponding PEC reactions. Fig. 2a indicates that the TiO_2 conduction band (CB) electrons may not be energetic enough to drive hydrogen evolution reaction, because the band structure is just a thermodynamic requirement but the sluggish reaction kinetics of photocatalytic hydrogen generation [16] requires a large overpotential. However, for the all-vanadium PEC storage cell shown in Fig. 2b, though the CB bottom of TiO_2 (around −0.5 V on the potential scale vs. NHE) seems not to be negative enough to drive the reduction reaction of $V^{3+} + e^- \rightarrow V^{2+}$ ($E_0 = -0.26$ V vs. NHE), fast electrochemical reaction kinetics of the vanadium ions [17], which is several orders of magnitude higher than that of H_2 evolution, may compensate the narrow potential window and result in a significant improvement in photocurrent.

The above analysis was confirmed by the PEC characterization of the storage cell in Fig. 3a. Different combinations of electrolytes in a two-electrode setup were studied using zero resistance ammetry method without external voltage bias. Upon illumination, immediately there appeared the photocurrents whose magnitudes were closely dependent on the type of electrolytes. The photocurrent using 0.1 M vanadium redox species as both anolyte and catholyte increased ca. 30% compared to that using 0.01 M, indicating that kinetics of adsorption/desorption and mass transport of the vanadium ions in the electrolyte, rather than their concentration, dominates the reactions. In addition, when the 0.1 M VO^{2+} and V^{3+} electrolytes in the all-vanadium PEC storage cell were replaced by 3 M H_2SO_4 at the photoanode (green curve in Fig. 3a) and cathode (black curve), respectively, a significant decrease of photocurrent was observed. For example, the photocurrent, taken at 120 s just before the air mass (AM) 1.5 filter was switched off, reduced 11.2 times when the catholyte was changed from 0.1 M V^{3+} to 3 M H_2SO_4 (the anolyte remained unchanged). This indicates that contribution of photocatalytic water splitting to the photocurrents measured from the all-vanadium PEC storage cell is negligible, even though very low molarities of vanadium ions (0.01 M and 0.1 M) were used.

Fig. 3b presents the cell voltages as a function of time. The measured voltage between the photoanode and Pt counter electrode was determined by the quasi-Fermi level of the TiO_2 and the redox potentials of the electrolytes. When the Pt counter electrode (cathode) was in contact with 3 M H_2SO_4, the cell voltage was, as expected, lower than that of the all-vanadium PEC storage cell since the thermodynamic potential of H_2O/H_2 (0.0 V vs. NHE) is higher than that of V^{3+}/V^{2+} (−0.26 V vs. NHE). On the other hand, when the VO^{2+} electrolyte was replaced with 3 M H_2SO_4 as the anolyte, the change in cell voltage was barely noticeable even though the thermodynamic potential of O_2/H_2O (1.23

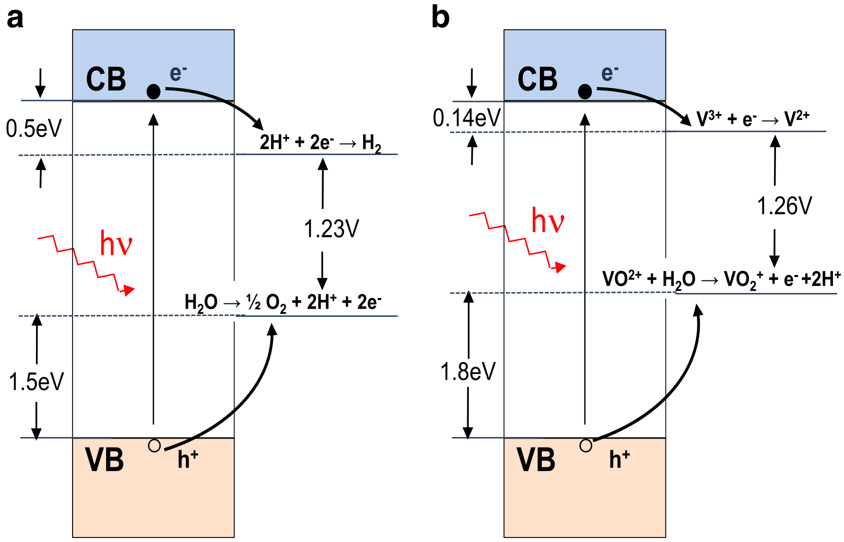

Fig. 2. Band positions of TiO_2 and corresponding PEC reactions in a) photocatalytic water splitting and b) an all-vanadium redox PEC storage cell. CB and VB refer to conduction band and valence band, respectively. The energy differences between the semiconductor band edges and thermodynamic redox reactions are indicated in the figures.