

Photorechargeable Properties of Metal Hydride-SrTiO₃ Electrode

Wen Kui ZHANG*, Xi Li TONG, Hui HUANG, Yong Ping GAN, Na HUANG

Department of Applied Chemistry, Zhejiang University of Technology, Hangzhou 310014

Abstract: A photosensitive metal hydride electrode was prepared by modification with perovskite-type SrTiO₃ photocatalyst. The photorechargeable properties of the prepared electrodes were investigated by using electrochemical cyclic voltammetry and EIS measurements. The results showed that the modified electrode exhibited the obvious photorechargeable properties. The reduction current increased remarkably under the xenon light irradiation compared with the unmodified electrode. During the photocharging process, the potential of the modified electrode shifted quickly to negative direction and a potential plateau of about -0.90V (*vs.* Hg/HgO) occurred at the end of light irradiation. The corresponding discharge capacity of the electrode was about 5.4 mAh/g.

Keyword: Perovskite catalyst, strontium titanate, photorechargeable properties.

Since Fujishima and Honda¹ discovered the effect of photosensitization of TiO₂ electrode on the electrolysis of water into H₂ and O₂, the photocatalysis by TiO₂ and other semiconductors has received much attention and been widely investigated. A series of novel photocatalysts including layered titanate², niobates³, perovskite materials and their pillared-products⁴ were discovered. Among these photocatalysts, perovskite-type SrTiO₃ oxide is an efficient photocatalyst. Recently, Akuto *et al.*⁵ constructed an interesting photorechargeable SrTiO₃-LaNi_{5-x}Al_xH_n | KOH | O₂ cell system. The light energy can be transferred into chemical energy and stored in the above cells. However, the corresponding electrochemical behaviors of the modified electrode and the mechanism were not investigated. In this paper, we will discuss photoelectrochemical properties of metal hydride-SrTiO₃ electrode.

Perovskite-type SrTiO₃ powder was prepared with Sr(NO₃)₂ and Ti(OBu)₄ materials using sol-gel technique. A commercial AB₅-type hydrogen storage alloy with the standard composition MmMn_{0.4}Co_{0.7}Al_{0.3}Ni_{3.4} was used for preparation of metal hydride electrode. The electrodes were prepared using dry powder compression technique without additives. SrTiO₃ oxide was dispersed in 10% PTFE suspension and dipped the metal hydride electrode into the suspension for several seconds, then dried at 60°C for 3 min. The above procedures were repeated for 5 times. Then the electrode was cool pressed at 10 MPa for 1 min. The electrode is 1.0 cm×1.0 cm×0.03 cm in size.

XRD analysis were carried out with a Thermo ARL SCINTAG X'TRA diffracto-

* E-mail: echem@zju.edu.cn

meter, using CuK_α radiation in the 2θ range from 10° to 70° with a scan rate of $2.4^\circ/\text{min}$.

The photoelectrochemical behaviors were measured in a conventional three-electrode electrolysis cell in which NiOOH was used the counter electrode, $\text{Hg/HgO}/6$ mol/L KOH as reference electrode, and the electrolyte was 6 mol/L KOH solution. All electrochemical measurements were performed by using a EG&G 273A potentiostat/galvanostat and a 5210 lock-in amplifier. The frequency ranged from 0.01 Hz to 100 kHz. A small ac signal of 10 mV in amplitude was used to perturb the system throughout the experiments. A 500W xenon lamp was used as the light source when measuring the photocharge characteristics. Before the electrochemical measurements, the electrodes were immersed into 6 mol/L KOH for 5h. The discharge current is about 6 mA/g, and the cut-off potential is set at -0.5V (vs. Hg/HgO) reference electrode. All experiments were performed at room temperature.

Figure 1 shows the XRD pattern of SrTiO_3 powder. As shown in **Figure 1**, the sample is composed of the single perovskite phase without other impurities. The lattice parameters calculated according to the diffraction data is $a=0.3916$ nm, which is in accordance with the standard value.

Figure 2 depicts the cyclic voltammograms of the metal hydride- SrTiO_3 electrode; the scan rate is 5 mV/s. As shown in **Figure 2**, a current peak occurs at about -0.57 V (vs. Hg/HgO), indicating the formation of H atom. The corresponding H oxidation peak occurs at about -0.65 V. When the potential is higher than -0.9V , the hydrogen evolves on the electrode. Under the xenon light irradiation, the cathodic reduction current peak

Figure 1 X-ray diffraction pattern for as-prepared perovskite-type SrTiO_3 oxide

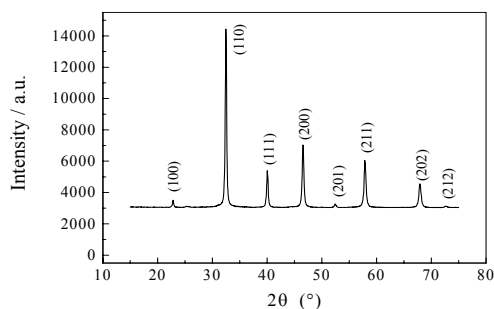


Figure 2 Cyclic voltammograms of metal hydride- SrTiO_3 electrode (Scan rate: 5mV/s)

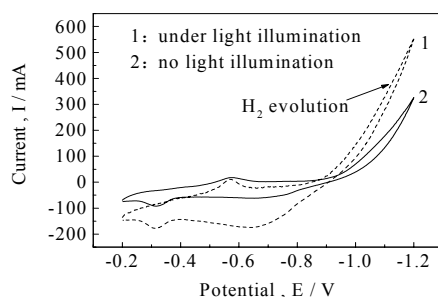
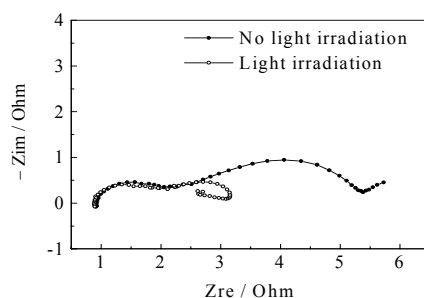
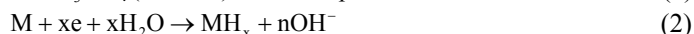
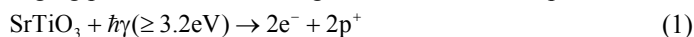


Figure 3 Nyquist plots of metal hydride-SrTiO₃ electrode

increased more quickly as the potential swiftd to negative direction, indicating that the light irradiation can remarkably improve the reduction current of water. The additional part of the reduction current may be ascribed to the photogenerated electrons which can react with water to produce hydrogen atom. However, the light irradiation has no influence in the reaction potential.

Figure 3 shows the electrochemical impedance spectrum of metal hydride-SrTiO₃ electrode. As shown in **Figure 3**, the electrochemical impedance spectrum is composed of two semicircles. The differences between two curves in the high frequency zone can be negligible but in the low frequency zone is very obvious. The semicircle appeared in the low frequency corresponds to the diffusion of hydrogen atom. Considering the photorecharging process, the following reaction would take place:



During photocharging process, the photogenerated electrons e excited into the conduction band are transferred to the active material. As a result, the electrons react with water to produce hydrogen atom, the produced H atom can be absorbed by the electrode bulk to form hydride. When the light is on, the remarkable shrinkage of semi-circle indicates that the solid diffusion of H atom becomes faster and more easy, *i.e.*, the reaction of eq. (2) is enhanced.

Especially, under the light irradiation, Nyquist plots of metal hydride-SrTiO₃ electrode show a special curved-shape in the low frequency zone. This may be ascribed to the adsorption of air on the surface of the electrode. During the photorecharging process, hydrogen will be produced as the following route:



The produced H atom combines into hydrogen and be adsorbed on the surface of the electrode, which induces the special bending of Nyquist plot in the low frequency zone.

Figure 4 illustrates the potential change as a function of the photocharging time for metal hydride-SrTiO₃ electrode. The curve indicates that the potential of metal hydride-SrTiO₃ electrode rises quickly with increasing of the photocharging time, then tend to a constant value, *i.e.*, a potential plateau of about -0.9V (*vs.* Hg/HgO) appears. At the first stage of light irradiation, the potential of electrode increases quickly, however, after about 150 mins, the potential tended to increase slowly with the increasing of time and a potential plateau appeared.

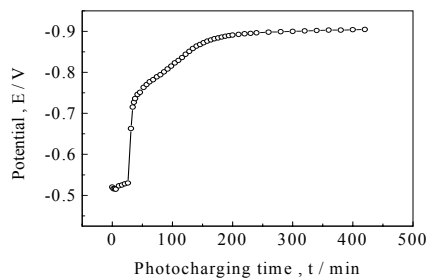
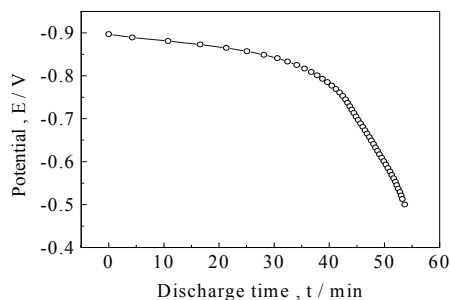
Figure 4 Photocharge curve of hydride-SrTiO₃ electrode**Figure 5** Discharge curve of metal hydride-SrTiO₃ electrode

Figure 5 presents the discharge curve of metal hydride-SrTiO₃ electrode. The corresponding discharge capacity of metal hydride-SrTiO₃ electrode was about 5.4 mAh/g at discharge current of 6 mA/g. Compared with the standard electrochemical capacity of the metal hydride electrode, the photorecharging capacity of the metal hydride-SrTiO₃ electrode is relatively small.

The experimental results show that the metal hydride electrode modified with perovskite-type SrTiO₃ photocatalyst can be photorecharged under the xenon light irradiation. Further investigations on the preparation of photocatalysts and the corresponding photoelectrochemical properties are still carried out.

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