



ELSEVIER

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Metal selenide films as the counter electrode in dye-sensitized solar cell

In Ae Ji^{a,1}, Hye Mi Choi^{a,1}, Jin Ho Bang^{a,b,*}

^a Department of Bionanotechnology, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Kyeonggi-do 426-791, Republic of Korea

^b Department of Chemistry and Applied Chemistry, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Kyeonggi-do 426-791, Republic of Korea

ARTICLE INFO

Article history:

Received 19 December 2013

Accepted 22 February 2014

Available online 3 March 2014

Keywords:

Metal selenides

Counter electrode

Dye-sensitized solar cell

Solar energy conversion

ABSTRACT

Various metal selenides were directly deposited on conductive glass and evaluated as counter electrodes (CEs) for dye-sensitized solar cells (DSSCs). Among the metal selenide films, NiSe₂, CoSe₂, and MoSe₂ were electrocatalytically active for I₃⁻ reduction, and, in particular, NiSe₂ was as efficient as the traditional Pt electrocatalyst. In comparison to its sulfide analog (NiS₂), NiSe₂ also exhibited a much better solar cell performance, which was ascribed to lower resistances to charge transfer and diffusion of electrolyte.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Since the pioneering work by O'Regan and Grätzel in 1991, DSSCs have received a great deal of attention as next-generation energy conversion systems due to their simple fabrication process and relatively high conversion efficiencies [1]. DSSCs comprise a photoelectrode (typically Ru-based dyes adsorbed onto mesoporous TiO₂ film) and a counter electrode (a thin electrocatalyst film for I₃⁻ reduction) assembled with an I⁻/I₃⁻ redox couple in between these two electrodes. Platinized conductive glass has long been utilized for CE because of the excellent electrocatalytic activity of Pt; however, the use of Pt has been considered a major factor affecting the cost competitiveness of DSSCs. Various alternatives have been proposed to address this issue, including metal sulfides, nitrides, carbides, and carbons [2–6]. A recent study also revealed that metal selenides could be utilized for CEs; however, only a few studies on metal selenides have been reported [7,8]. In addition, most of the Pt-free electrocatalysts are synthesized as fine powders, and are thus subjected to post-treatments (mixing with binders or annealing) to be used for CEs. These additional processes often lead to an aggregation of particles and hinder the full utilization of the electrocatalyst. Therefore, the development of a direct deposition method onto conductive glass that can be easily generalized for various electrocatalysts would be of great benefit.

In this study, we directly deposited various metal selenides on F-doped SnO₂ (FTO) glass by a facile, low-temperature process—a successive ionic layer adsorption and reaction (SILAR) method—and examined their feasibility as CEs in DSSCs. NiSe₂ deposited as a one-dimensional array was as efficient as Pt among the metal selenides we investigated and was superior to its sulfide counterpart, NiS₂, due to its lower interfacial resistance.

2. Experimental section

For the fabrication of metal selenide CEs, FTO glass (Pilkington TEC-15) was dipped in an aqueous KOH solution (0.5 M) for 1 h. The FTO glass was then alternately immersed for 30 s under N₂ atmosphere into metal chloride solutions (30 mM) in ethanol (for MnSe and PbSe, metal acetates were used) and Se²⁻-containing solution (30 mM) prepared by reducing SeO₂ with two equivalents of NaBH₄ in ethanol. The SILAR cycles were repeated 12 times for complete coverage. For the preparation of NiS₂ CE, Na₂S solution (30 mM) was used as a sulfur source. For the fabrication of Pt CE, Platisol S/TP (Solaronix) was doctor-bladed onto FTO glass and annealed at 450 °C for 30 min. The detailed solar cell fabrication process was presented in a previous report [9]. Briefly, photoelectrodes with B2 (N719) dye (Dyesol) adsorbed on a 12-μm-thick TiO₂ film (Ti-Nanoxide T/SP (Solaronix) and DSL 18NR-AO (Dyesol) pastes screen-printed on FTO glass) were assembled into a sandwich-type cell with various CEs and EL-HPE (Dyesol) electrolyte. For Tafel and electrochemical impedance spectroscopy (EIS) measurements, symmetric dummy cells were prepared by assembling two identical CEs.

* Corresponding author. Tel.: +82 31 400 5505; fax: +82 31 400 5457.

E-mail address: jbang@hanyang.ac.kr (J.H. Bang).

¹ These authors contributed equally to this work.

X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (Rigaku D/Max-2500/PC). Scanning electron microscopy (SEM) was carried out using a field-emission scanning electron microscope (Hitachi S-4800). A solar simulator (HAL-320, Asahi Spectra) was employed as a light source, and photocurrent–photovoltage (J – V) curves were recorded using a Keithley 2400 source meter under illumination of AM1.5G simulated solar light. A potentiostat (CH Instruments, CHI 660D) was employed to perform EIS and Tafel measurements. EIS spectra were measured under a frequency range of 0.1 Hz–100 kHz and a perturbation amplitude of 10 mV, and Tafel polarization curves were obtained at a scan rate of 50 mV/s.

3. Results and discussion

SILAR was found to be versatile for the direct deposition of thin metal selenide films on FTO glass because various selenides could be quickly deposited by changing only the metal cation solutions [10]. In this work, seven different types of metal selenides were prepared by SILAR, and their electrocatalytic activity for I_3^- reduction ($I_3^- + 2e^- \rightarrow 3I^-$) was examined by Tafel polarization curve measurement. Fig. 1A shows that the exchange current densities of NiSe₂, CoSe₂, and MoSe₂ were higher than those of other selenides, suggesting that these selenides are potentially useful for CEs.

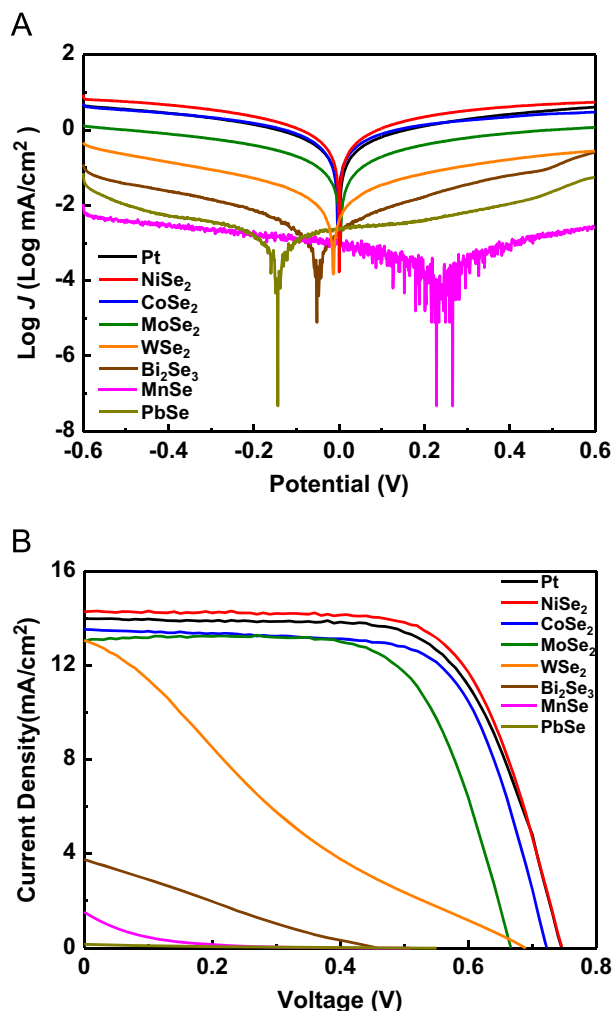


Fig. 1. (A) Tafel polarization curves of various metal selenide electrodes and (B) J – V curves of DSSCs when metal selenides were used for CEs.

When utilized as CEs in a DSSC, this observation was indeed reflected in the J – V curve measurements (Fig. 1B). The solar cell performance with the NiSe₂ CE was slightly higher than that with Pt CE, whereas the DSSCs with the CoSe₂ and MoSe₂ CEs showed lower efficiencies than those with Pt. EIS measurements were carried out to elucidate the electrochemical properties of these selenides. Nyquist plots and an equivalent circuit, from which EIS parameters are extracted, are presented in Fig. 2A, and the EIS parameters (R_s , R_{ct} , and Z_w) are summarized in Table 1. R_s values of all CEs were similar, suggesting that the differences in the electrocatalytic activity mainly stemmed from R_{ct} and Z_w . The R_{ct} and Z_w of NiSe₂ were much smaller than those of CoSe₂ and MoSe₂, indicating that charge-transfer takes place at a relatively fast rate, and diffusion of the electrolyte also occurs efficiently on the NiSe₂ CE compared to other selenides. To exclude the effect of any impurities that may affect R_{ct} , XRD analysis (Fig. 2B) was conducted, which revealed that all the diffraction peaks match the standard CoSe₂ (JCPDS 09-0234), MoSe₂ (JCPDS 29-0914), and NiSe₂ (JCPDS 41-1495). We therefore concluded that the observed disparity in R_{ct} values originated from metal selenides' own electrocatalytic properties. To determine the reason for different Z_w values, the morphologies of each CE were examined by SEM because the diffusion of electrolyte is mainly governed by the porous structure of electrodes [11]. The SEM images in Fig. 2C–F reveal that each CE possesses different morphologies; myriads of one-dimensional nanobelts were vertically aligned in the NiSe₂ CE, whereas nanoparticles or octahedra-shaped microparticles were severely agglomerated in the CoSe₂ and MoSe₂ CEs, respectively. We speculate that the one-dimensional arrays of the NiSe₂ CE could provide more internal space for the effective mass transport of electrolyte, thus reducing the diffusion resistance. The finding that the NiSe₂ CE has the smallest Z_w value partly supports this hypothesis.

While many metal chalcogenides have been reported as non-Pt based electrocatalysts, there have been no studies comparing sulfides with selenides. Since the physiochemical properties of binary metal chalcogenides are subtly dictated by the types of chalcogen (e.g., S and Se) that metal cation combines with [12], it would be interesting to investigate the effect of anions on the electrocatalytic activity of metal chalcogenides for the I_3^- reduction. For this purpose, NiS₂ CE was prepared as a counterpart of the NiSe₂ CE by the SILAR method. XRD analysis (Fig. 3A) shows that both NiS₂ and NiSe₂ were pure and crystalline. Interestingly, the SEM image (Fig. 3B) of NiS₂ reveals that the NiS₂ CE was composed of micrometer-sized, truncated cubes. Given that variously shaped metal chalcogenides, such as nanobelts (NiSe₂), nanoparticles (CoSe₂), octahedra (MoSe₂), and cubes (NiS₂), can be formed by the SILAR method, we believe that SILAR can be further developed for the preparation of a wide variety of nanostructured metal chalcogenides, which is the focus of our ongoing research. When employed in DSSCs as CEs, NiS₂ was found to be inferior to NiSe₂. Fig. 3C displays the J – V curve of DSSCs with the NiS₂ and NiSe₂ CEs, showing that the low FF played a major role in deteriorating the solar cell performance. To obtain greater insight into the NiS₂ CE, EIS analysis was carried out. Fig. 3D exhibits the Nyquist plots obtained from the NiS₂ and NiSe₂ CEs, from which EIS parameters (Table 1) were extracted using the equivalent circuit shown in Fig. 2A. All interfacial resistances of the NiS₂ CE were found to be higher than those of the NiSe₂, and the Z_w of the NiS₂ CE was, in particular, much higher, which is ascribed to the compact NiS₂ film composed of micrometer-sized cubes that may hinder the diffusion of electrolyte. In addition to the difference in morphology, the film thickness may also affect the Z_w values. The film thicknesses of both CEs were found to be quite different: 3–4 μ m for NiSe₂ and 6–7 μ m for NiS₂, which reflects different attachment affinity of S and Se during the SILAR synthesis. The thicker NiS₂ film

Download English Version:

<https://daneshyari.com/en/article/1644293>

Download Persian Version:

<https://daneshyari.com/article/1644293>

[Daneshyari.com](https://daneshyari.com)