THE PEC AS AN EASY-TO-PREPARE AND CHEAPER ALTERNATIVE POWER SOURCE

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Abstract: Porous CdSe photoelectrochemical converter is fabricated and tested using highly porous substrate of metallic Cd. Following mean PEC characteristics obtained: efficiency: 5%. On the other hand, CdSe semiconductor developed on the highly porous (60%) cadmium substrate showed some 2% of efficiency with high dark current value only. It was shown that the light-sensitive phase is monoclinic 2 corresponding to Cd0.53Se0.47 formula determined by the X-Ray, SEM and elementary analysis tool methods.

Keywords: CdSe PEC, porous semiconductor electrode, semiconductor film

1. Introduction

Coming from the worldwide harsh ecological situation, nowadays more and more attention induce alternative power sources, an example of which is the photoelectrochemical converter (PEC). Semiconductor solar converters are widely known power sources capable directly to convert light energy into electrical one. The unique properties of cadmium-chalcogenide compounds (CdS; CdSe; CdTe and their mixed alloys), such as direct transition, optimal bandgap width (1.35-1.85 eV) etc., attracted immense interest for the use in PEC. On the other hand, electrochemically fabricated semiconductor films are salient by their ease-of-technology and low-cost virtues. Besides, electrochemically fabricated semi-conductor layers can be produced with any given surface area and form, as they are polymorphic and usable in PECs. Conventionally, CdSe semiconductor films are obtained by the potentiostatic tool method, which has two inherent drawbacks: first, it is impossible to contain the layer thickness as the cadmium ions are co-deposited at diffusion limiting current density values; and secondly, the devised PEC with CdSe semiconductor exhibited poor reproducibility and below-par light conversion efficiency. It was possible to produce CdSe semiconductor light-sensitive electrodes by the precipitation of selenium on the pre-developed porous cadmium carrier galvanostatically [1]. On the other hand, substitution of Ti-metal or Ni-metal used as conventional substrates with Cd-metal improves both the CdSe PEC output characteristics (over 4.5% with practically no dark current) and the reproducibility as well, as it was shown in [2]. Developed technology permits to obtain highly porous semiconductor electrode predominantly having open pores. It is known that porosity increases PEC efficiency and, at the same time, permits to reduce PEC cell power losses incurred within the cell (re the [2]). Cd0.53Se0.47 phase formation was confirmed by SEM and elemental analysis methods.

2. Experimental

Electrochemical workstation 600 brand Potentiostat (CH Instruments, USA) has
have been used both for the development of CdSe films and for cutting the main photoelectrochemical parameters. Platinum wires served as reference and counter electrodes. Collimated 100 W halogen lamp was the source of light at 65 mW/cm² intensity. The used technique is described elsewhere, for example in [3]. Experiments were carried out in the quartz cell.

On Fig 1 the typical volt-ampere characteristic is presented from which one can determine main PEC characteristics: open circuit voltage, $V_{OC}$; short circuiting current density, $I_{SC}$; dark current, and fill factor, $V_m*I_m/V_{OC}*I_{SC}$.

RedOx electrolyte has the following formulae: NaOH : S : Na₂S = 1 : 1 : 1 in M. The calculated thickness of CdSe coating was circa 0.5 μm. RedOx electrolyte has the following formulae: NaOH : S : Na₂S = 1 : 1 : 1 in M.

Rotating disc electrode (dia is 5 mm at 800 rpm) was used for non-porous CdSe film obtainment. Se bath formula is 4 mM SeO₂, pH = 2.2 T = 90 °C, t = 4 min, j= 1.2 mA/cm².

Porous CdSe were prepared according to the technology developed for the fabrication of pasted Cd electrodes based on polyvinyl butyral (PVB) binder [4]. Porosity of the electrodes was determined by the BET method and lies within 55–65%.

Further development of the Se layer on the surface – and partially within the pores of the Cd electrode – was performed as is described in our previous works [4,5].

Scanning electron microscopy (SEM) images were taken on Vega©Tescan instrument.

3. Results and discussion

On figure 2 the typical Volt-Ampere characteristic is presented for the flat (non-porous) CdSe PEC obtained by the rotating disc electrode method.

![Figure 2. RDE output in polysulfide Redox electrolyte](image)

Please note that this figure curve is reversal of the Fig. 1.

For the RDE case we have practically no dark current as one could easily see from the curve pattern depicted on Fig. 2.

On Fig. 3 the same plot for the porous PEC is provided.

![Figure 3. Porous CdSe output in polysulfide Redox electrolyte](image)

Here, as opposed to RDE experiments, we have increased dark current and lower output. Actually, this is a result of poor Se deposition inside the pores of the Cd-metal.
substrate serving as active short-circuiting centers of the PEC. This is hard-to-overcome technological issue with regard to porous systems and our further investigations are focused on the use of forced convection to cover the inner pores of Cd substrate with CdSe layer.

On Figure 3 the electron-microscope images of semiconductor CdSe porous film are presented.

Figure 4. SEM images of the semiconductor CdSe porous film
Magnifications: a. 10220x, b. 3950x, c. 1000x.

As Fig. 3c shows, the produced porous layers are homogenous with even distribution of the binder (PVB) throughout the porous structure. According to Fig. 3a, the diameter of the main pores is Ca 2 µm. The results of an elementary analysis are presented in the Table.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>13.38</td>
<td>43.23</td>
</tr>
<tr>
<td>Na</td>
<td>4.55</td>
<td>10.23</td>
</tr>
<tr>
<td>S</td>
<td>3.20</td>
<td>5.15</td>
</tr>
<tr>
<td>Se</td>
<td>26.36</td>
<td>17.25</td>
</tr>
<tr>
<td>Cd</td>
<td>52.51</td>
<td>24.14</td>
</tr>
</tbody>
</table>

As it follows from the table, the mass content of sulfur is 3.2% which inculcates into the electrode structure due to presence of free Cd on the surface of the electrode to produce CdS. This is a non-direct proof of the presence of metallic phase on the CdSe porous structure which is the main culprit of deterioration of the characteristics’ of the porous PEC.

On the other hand, the mass ration of Cd and Se in the semiconductor is 21.2/19.2, respectively if we exclude Se in-electrode structure invasion. This result corresponds to Cd$_{0.53}$Se$_{0.47}$ which is close to of light-sensitive monoclinic 2 phase composition.

Conclusion

Experiments show that it is possible to develop CdSe light-sensitive phase electrochemically corresponding to monoclinic 2 phase on the highly-porous substrate. Higher porosity not only increases the light response of the PEC due to band bending of the CdSe semiconductor, but the porous structure could lead to PEC overall output power enhancement thanks to reduced voltage drop in the electrolyte. This is because, in this PEC configuration, the counter electrode could be positioned directly behind the semiconductor electrode as it has open-ended pores with Redox ions’ shorter run path in between the light-sensitive and counter electrode.

References