Research Article

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The structure and conductivity of polyelectrolyte based on MEH-PPV and potassium iodide (KI) for dye-sensitized solar cells

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Abstract: This article presents the results of a research on the effects and properties of the potassium iodide additive onto the structure of the MEH-PPV polymer material, in its aspect of application in the dye-sensitized solar cell. Changes in MEH-PPV surface morphology were researched through increasing of the potassium iodide content measured by scanning electron microscope. The increased content of potassium iodide also led to increased electrical conductivity measured by the Keithley meter. The electrical properties of the dye-sensitized solar cell were also studied, in which the liquid electrolyte was replaced with a thin layer of polyelectrolyte, based on MEH-PPV and potassium iodide.

Keywords: MEH-PPV; Polyelectrolyte; Dye-sensitized solar cells

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1 Introduction

Electrolyte, which is filling the interface between a semiconductor layer and a counter electrode in the dye-sensitized solar cell (DSSC), is usually a solution containing a I⁻/I₃⁻ redox system. The task of the electrolyte is to transfer the electron to the oxidized dye, so that it returns to its basic state. The first liquid electrolyte used in the dye-sensitized solar cells was the LiI/I₂. Currently, the most common and most effective electrolyte is the liquid electrolyte based on redox compound iodide/triiodide containing various organic solvents such as: acetonitrile, ethylene carbonate, 3-methoxy propionitrile and N-methylpyrrolidone[1–4]. In the DSSC ionic liquids are also being used, i.e. liquids composed only of ions. Nowadays, the mentioned ionic liquid is understood as a salt in liquid form having a melting temperature not exceeding 100 °C. The disadvantage of liquid electrolyte is its ability to evaporate and leak. This results in a significant reduction in the life time and efficiency of dye-sensitized solar cells. There was an intensification of research into the replacement of liquid electrolyte. One solution is to use a material with ionic conductivity (so called Hole Transport Material – HTM). The first studies concerned inorganic materials such as CuI, CuBr, or CuSCN. However, despite the good conductivity of these materials (10⁻² S/cm), the stability of the solar cells prepared with them, is very poor [4–6]. Currently, the search for the successor of liquid electrolyte is being intensified towards the development of ionic conductive organic materials. Examples of use of various types of ion-conductive materials and their effect on DSSCs are shown in Table 1 [7–19].

The research presented in this paper focuses on the appropriate doping of the MEH-PPV polymeric material by...
adding potassium iodide to improve its electrical conductivity and the development of thin film deposition technology for use in dye-sensitized solar cells.

2 Materials and methodology

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], anhydrous potassium iodide (KI) and other chemicals were supplied by Sigma Aldrich. MEH-PPV is a conductive polymer with a width energy band gap equal 2.7 eV and red color, often used for the production of OLEDs with bright light. MEH-PPV is a derivative of PPV, which due to its asymmetric side chains is highly soluble in most organic solvents. N-Methylpyrrolidine (NMP) was used to dissolve the polymer and salt, and the liquid solutions were spin-coated to form polyelectrolyte thin films. Scanning Electron Microscopic (SEM) images were taken with a Zeiss Supra 35. Qualitative studies of chemical composition were also performed using the Energy Dispersive Spectrometer (EDS). The resistance of the prepared samples was measured using a Keithley meter. The meter was connected to a specialized adapter for testing thin films. Silver contacts connected to external electrodes was applied on the edge of the layer to a better connection and more accurate measurement. Resistance measurements were made using constant voltage measuring in real time of the running current. In order to test the suitability of developed materials for application in the construction of photovoltaic cells, a series of dye-sensitized solar cells ITO/TiO2/dye/active layer/Al were prepared. The active layer is made from pure MEH-PPV and doped with potassium iodide. Current-voltage characteristics of dye-sensitized solar cells were measured on a glass substrate with ITO electrodes. Silver contacts connected to external electrodes was applied on the glass substrate, additionally shows reflects from potassium iodide in the form of KI precipitates slightly above 100 nm (Figure 1c). With participation of the 15% of KI, large crystals of potassium iodide were recorded (even above 2 µm). In addition, with the present precipitates, regular agglomerates of polymeric material with characteristic oval shapes had appeared (Figure 1d).

There was also provided a qualitative analysis by using energy dispersive spectrometry. Documented spectrum with reflections typical for carbon (0.277 keV) and oxygen (0.525 keV), which is provided from the MEH-PPV polymer layer and the carbonate (1.067 keV), silicon (1.739 keV) and calcium (3.689 keV) derived from the glass substrate (Figure 2a). The EDS spectrum of the MEH-PPV polymer dissolved in NMP solvent with 5% KI deposited on a glass substrate, additionally shows reflects from potassium (3.311 and 3.588 keV) and iodine (3.936 and 4.219 keV) (Figure 2b). Distribution maps of elements detected in the analyzed area of the MEH-PPV were made (Figures 3a-f). Uniform distribution of potassium iodide in the structure of the polymer MEH-PPV was recorded.

The resistance of the prepared samples was measured using a Keithley meter. The meter was connected to a specialized adapter for testing thin films. Measurement of volume resistance of the MEH-PPV polymer layer was measured on a glass substrate with ITO electrodes. Silver contacts connected to external electrodes was applied on the edge of the layer to a better connection and more accurate measurement. Resistance measurements were made using a constant voltage measuring in real time the current running. The average value of the measured resistance was equal 6.26·10⁸ Ω (Table 2). The conductivity of the non-doped MEH-PPV layer was equal 2.47·10⁻¹¹ S·cm⁻¹. The additive 5% potassium iodide reduced the resistance to 2.33·10⁸Ω. The conductivity of the doped polymer increased to 5.86·10⁻⁹ S·cm⁻¹, which is two orders of magnitude. The layer with 10% KI was characterized by a average value of measured resistance equal 3.45·10⁻⁸Ω. Conductivity increased to values of 4.68·10⁻⁸ S·cm⁻¹. The addition of 15% potassium iodide resulted in a significant decrease in the measured resistance and its average value was 5.50·10⁻⁸ Ω. The conductivity of the thin layer of the polymer PVDF-HFP with the additive of 15% KI was 2.69·10⁻⁶ S·cm⁻¹.

3 Results and discussion

The surface of the MEH-PPV polymer layer dissolved in a NMP solvent deposited on a glass substrate was made in SEM at 50 000 magnification (Figure 1a). Only with such large magnification uniform structure had been recorded. There are no visible cracks or any precipitates.
Figure 1: SEM image of MEH-PPV polymer layer with KI content: a) 0%; b) 5%; c) 10%; d) 15%

Figure 2: EDS spectrum of MEH-PPV polymer layer with KI content: a) 0%; b) 10%
The structure and conductivity of polyelectrolyte based on MEH-PPV

Figure 3: Distribution maps of elements detected in the analyzed area of the MEH-PPV with 10% content of KI

Table 2: Conductivity of MEH-PPV thin film with different KI contents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average value of measured resistance [Ω]</th>
<th>Conductivity [S·cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEH-PPV</td>
<td>6.26·10^8</td>
<td>2.47·10⁻¹¹</td>
</tr>
<tr>
<td>MEH-PPV + 5%KI</td>
<td>2.33·10^6</td>
<td>5.86·10⁻⁹</td>
</tr>
<tr>
<td>MEH-PPV + 10%KI</td>
<td>3.45·10^5</td>
<td>4.68·10⁻⁸</td>
</tr>
<tr>
<td>MEH-PPV + 15%KI</td>
<td>5.50·10³</td>
<td>2.69·10⁻⁶</td>
</tr>
</tbody>
</table>

Table 3: Electrical properties of produced solar cells determined on the basis of the measured light current-voltage characteristics

<table>
<thead>
<tr>
<th>Solar cell</th>
<th>U_OC [mV]</th>
<th>I_SC [mA]</th>
<th>U_max [mV]</th>
<th>I_max [mA]</th>
<th>P_max [mW]</th>
<th>FF</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEH-PPV</td>
<td>609.64</td>
<td>4.81</td>
<td>347.81</td>
<td>3.56</td>
<td>1.2</td>
<td>0.43</td>
<td>2.02</td>
</tr>
<tr>
<td>MEH-PPV+5%</td>
<td>589.73</td>
<td>3.85</td>
<td>404.21</td>
<td>3.14</td>
<td>1.3</td>
<td>0.56</td>
<td>2.04</td>
</tr>
<tr>
<td>MEH-PPV+10%</td>
<td>629.68</td>
<td>5.04</td>
<td>419.94</td>
<td>3.92</td>
<td>1.6</td>
<td>0.52</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Current voltage characteristics were measured (Figure 4) from which the open circuit voltage, short circuit current, fill factor, maximum power and efficiency were calculated (Table 3). The software used to calculate the solar cell parameters takes into account the intensity of the intensity of solar radiation incident on the solar cell and solar cell surface. The following mathematical formula was used:

\[ E_{ff} = FF \frac{U_{oc}I_{sc}}{P_{opt}} = FF \frac{U_{oc}I_{sc}}{P_{in}A_0} \]

where: \( P_{in} \) – intensity of solar radiation incident on the solar cell; \( A_0 \) – solar cell surface.

A solar cell containing a layer of non-doped polymer MEH-PPV in its structure is characterized by a maximum power of 1.2 mW and an efficiency of 2.02%. The addition of 5% potassium iodide influenced especially on the increase of fill factor to 0.56. Thanks to that, the maximum power of the solar cell is equal to 1.3 mW and the efficiency 2.04%. For a solar cell with a MEH-PPV and an additive of 10% KI the maximum power was 1.6 mW, while the efficiency 2.74%. It was not decided to make a solar cell with a MEH-PPV layer containing 15% KI because large KI precipitation caused its instability, despite its conductivity increased with higher content of potassium iodide. The dif-
different concentration of KI was influenced on resistivity of the MEH-PPV thin film and on efficiency of the prepared solar cell (Figure 5).

![Figure 4: Light current-voltage characteristics of produced solar cells](image)

![Figure 5: The influence of the different concentration of KI on resistivity of the MEH-PPV thin film and on efficiency of the prepared solar cell](image)

4 Conclusions

Doping the MEH-PPV polymeric material with potassium iodide generates a large number of charge carriers causing an increase in its electrical conductivity. After adding 10% KI to MEH-PPV, its conductivity is increased by 3 orders of magnitude (from $2.47 \times 10^{-11}$ to $4.68 \times 10^{-8}$), and after adding 15% KI by 5 orders of magnitude (from $2.47 \times 10^{-11}$ to $2.69 \times 10^{-6}$). On the basis of the surface morphology, it was determined that the polyelectrolyte based on the MEH-PPV may comprise a maximum of 10% potassium iodide. Above this content, there are present large salt crystals, causing discontinuity of the thin layer. Of all the newly developed solar cells, the highest efficiency of 2.64% has a cell with a MEH-PPV polymer doped with 10% of potassium iodide.

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References


