A CARBON-NANOTUBES COUNTER ELECTRODE FOR FLEXIBLE DYE-SENSITIZED SOLAR CELLS

ELEKTRODA IZ OGLJIKOVIH NANOCEVK ZA TANKOPLASTNE BARVNO OBČUTLJIVE SONČNE CELICE

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1 INTRODUCTION

The utilisation of renewable energies is of significant importance because of the increase in fossil energy costs in combination with carbon dioxide reduction preventing global warming. The importance of solar energy can be considered as a sustainable energy that may successfully satisfy a part of the energy demand of future generations.1,2 Photovoltaics seems to be the most promising new electric energy source. What is needed to transform solar power from a marginalised technology to a mainstream source of energy is cheaper materials. At present, the main scientific effort is made to lower the production costs of PV systems and improve their parameters. It is believed that in the not so distant future, thanks to new materials, solar cells could be ubiquitous and one of the cleanest energy sources all over the world.3,4 There are many publications about the methods of shaping the surface and structure of materials to improve their properties.5–12 Some materials exhibit a property known as the photovoltaic effect that causes them to absorb photons of light and excite an electron or other charge carrier to a higher-energy state. When these free electrons are captured, an electric current results that can be used as electricity. In recent years, most of the solar cells are based on a silicon substrate.11–15 Although the cost per peak watt of crystalline silicon solar cells has significantly dropped, it is still expensive compared to the conventional grid electricity resources.15 Dye-sensitized solar cells (DSSCs) are an inexpensive alternative to the conventional p-n junction solar cells. The use of DSSCs is one of the most promising approaches towards the realisation of both high performance and low cost, thanks to their low material cost and ease of manufacturing.16–18 One of the challenges of this technology is, however, expensive, the heavy and non-elastic glass substrate typically used in DSSCs. Therefore, scientists transfer the DSSC technology from glass substrates to lightweight, cost-efficient, and flexible plastic foils and metal sheets. Additionally, flexible dye-sensitized solar cells built on elastic substrates have
Attracted great industrial interest because they can be roll-to-roll printed, which is well suited for scale mass production (accelerate production and reduce cost).19–21

In this paper we report on flexible DSSCs based on a carbon-nanotubes counter electrode. The influence of mechanical stress arising from the bending of the flexible substrate on the quality and resistance of the deposited layers was investigated.

A fundamental property of insulators is resistivity. The resistivity can be used to determine the dielectric breakdown, dissipation factor, moisture content, mechanical continuity and other important properties of the material. The volume resistivity of some materials, such as sapphire and Teflon®, can be as high as $10^{16}$ to $10^{18}$ Ohm-cm. Because of such large magnitudes, measuring the resistivity of insulators can be difficult unless proper test methods and instrumentation are used. One test method often used for measuring the resistivity of materials is ASTM D-257, "DC Resistance or Conductance of Insulating Materials." Instruments called electrometers are used to make this measurement because of their ability to measure small currents. Two methods are mostly used to measure high resistance, i.e., the constant-voltage method and the constant-current method.22–23

In the constant-voltage method, a known voltage is sourced and a picammeter or electrometer ammeter is used to measure the resulting current. The basic configuration of the constant-voltage method is shown in Figure 1. In this method, a constant-voltage source, $V$, is placed in series with the unknown resistor, $R$, and an electrometer ammeter, $A$. Since the voltage drop across an electrometer ammeter is negligible, essentially all the voltage appears across $R$. The resulting current is measured by the ammeter and the resistance is calculated using Ohm’s law, $R=\frac{V}{I}$.23–24

In the constant-current method, a constant current is forced through the unknown resistance and the voltage drop across the resistance is measured. The basic configuration for the constant-current method is shown in Figure 2. Current from the constant-current source, $I$, flows through the unknown resistance, $R$, and the voltage drop is measured by the electrometer voltmeter, $V$. Using this method, resistances up to about $10^{14}$ Ohm can be measured. Even though the basic procedure seems simple enough, some precautionary measures must be taken.22–24

One of the components in dye-sensitized solar cells is the counter electrode. The role of the counter electrode is to act as a catalyst for reducing the redox species, which are the mediators for regenerating the sensitizer after the electron injection, or for collecting the hole from the hole-transporting materials.25–28 This paper presents the influence of mechanical stress arising from the bending of a flexible substrate on morphology, the resistance of the counter electrode based on carbon nanotubes with the addition of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) PEDOT:PSS and polyvinylpyrrolidone PVP as well as electrical properties of dye-sensitized solar cells.

2 EXPERIMENTAL PART

Multi-walled carbon nanotubes (MWCNTs) were dispersed in anhydrous ethyl alcohol using ultrasonic dispersion methods. Then the poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) PEDOT:PSS was added. Carbon nanotubes are materials that strongly agglomerate. Therefore, they were exposed to dispersion for 45 min. To prevent the aggregation of carbon nanotubes, the mixture of 95% of mass fractions of active material and 5% of mass fractions of polyvinylpyrrolidone PVP was used. Using a spin coating methods, the mixture was deposited on the polymer polyethylene terephthalate (PET) with a thin layer of indium tin oxide (ITO) and dried at 60 °C for 25 min. The platinum thin film was deposited on a PET foil in a device based on the sputtering method (Physical Vapour Deposition – PVD) in an Ar atmosphere. The sputtering time was 90 s, the current was 50 mA and the voltage was 50 V.

The photoelectrode was prepared on a flexible ITO-PEN substrate by a doctor-blade technique using a commercially available TiO2 nanocrystalline powder P 25 Degussa mixed with ethyl alcohol and distilled water. After that the films were sintered at 120 °C for 4 h. The photoelectrodes were immersed in the anhydrous ethanol solution of 0.5-mM N3 (Cis-dioiothyocyanato-bis(2,2’-bipyridyl-4,4’’-dicarboxylic acid) ruthenium(II), Solaronix) for 24 h at room temperature. The internal space between the photoanode and the counter electrode was controlled at 25 μm by Surlyn foil (Solaronix). The photoanode and counter electrode were sealed with a 25-μm-thick Surlyn frame at 100 °C for 15 s. After sealing the cells were filled with the electrolyte solution.

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with redox couple $\text{I}^-/\text{I}_3^-$ through the hole in a counter electrode.

The influence of the mechanical stress arising from the bending of the flexible substrate on the quality and resistance of counter electrode based on carbon nanotubes with the addition of PEDOT:PSS and PVP. The samples were bent with the tester for measuring the bending strength of polymeric materials (Figure 3).

The morphology of the counter electrodes based on platinum and carbon nanotubes deposited on a PET foil was performed using a scanning electron microscope (Zeiss Supra 35). In order to obtain images of the surface topography, the detection of secondary electrons by the detector In Lens was used.

The resistance of the prepared samples was measured using a Keithley meter. The meter was connected to a specialised adapter for testing thin films. This was in order to better contact and more accurately measure on the edge of the layers applied silver contacts connected to external electrodes. The measurement block diagram used for our measurements is presented in Figure 4.

Resistance measurements were made using a constant-voltage measurement in real time with the current running. The chosen method allows us to obtain reliable results only for layers deposited on a polymer foil. It can be assumed that the resistance of the layers is the same or similar, regardless of the substrate.

Electrical parameters of manufactured flexible dye-sensitized solar cells with counter electrode based on platinum and carbon nanotubes with the addition of PEDOT:PSS and PEDOT:PSS/PVP were characterised by measurements of I-V illuminated characteristics on PV Test Solutions Tadeusz Żdanowicz Solar Cell I-V Tracer System under standard test condition (AM 1.5, 1000W/m$^2$). The level of irradiance was determined using the reference cells with a KG5 filter.

The construction of flexible dye-sensitized solar cells is illustrated in Figure 5.

The structure of produced DSSCs consists of components:
- working electrode – dye molecule (N3) coated nanocrystalline porous TiO$_2$ deposited on PET/ITO substrate,
- counter electrode – carbon nanotubes with the addition of PEDOT:PSS and PVP deposited on PET/ITO substrate,
- electrolyte (Iodolyte Z-150, Solaronix) containing an $\text{I}^-/\text{I}_3^-$ redox couple.

3 RESULTS AND DISCUSSION

Figure 6 shows the morphology of the PET/ITO foil coated with the Pt film. It illustrates that the substrate is uniformly covered with the Pt film.

A detailed inspection of scanning electron microscope micrographs of PET/ITO foils coated with the Pt film after bending revealed microcracks and crevices (Figure 7). This indirectly indicates that platinum film...
Figure 6: SEM images of platinum on PET/ITO foil

Figure 7: SEM images of platinum on PET/ITO foil after 100 bending cycles

Figure 8: SEM images of counter electrode based on carbon nanotubes with addition: a) PEDOT:PSS/PVP, b) PEDOT:PSS after 100 bending cycles

Figure 9: SEM images of counter electrode based on carbon nanotubes with addition PEDOT:PSS/PVP after 100 bending cycles
can have poor properties for catalytic activity at the counter electrode and electrical conductivity for the charge transfer. The cracks are formed mainly along the bending line. Moreover, the PET foil coated with ITO and Pt after 100 bending cycles in some places delaminates and breaks away from the elastic substrate (Figure 7).

Figure 8 shows the SEM images of a counter electrode based on carbon nanotubes with the addition of PEDOT:PSS and PEDOT:PSS/PVP. The addition of 5% of mass fractions of polyvinylpyrrolidione PVP prevents the agglomeration of carbon nanotubes. It was observed that, after the same number of bending cycles, the surface of the counter electrode based on carbon nanotube with the addition of PEDOT:PSS/PVP is much more damaged than the surface of the counter electrode without PVP (Figures 9 and 10). However, the amount of damage and the size of the defects in the carbon-nanotubes counter electrode is much smaller than in the platinum foil. It can be seen that carbon nano-elements reduce the spread of cracks.

The resistance of the carbon-nanotubes thin films with the addition of the PEDOT:PSS polymer was about $4 \cdot 10^3 \Omega$ (Figure 11). The appearance of small cracks registered using a scanning electron microscope did not affect significantly the results of electrical measurements. Mechanical stress caused by the bending of the substrate slightly affected the resistance of the tested layer. After 50 cycles of the bending, the resistance value increased to about 5.08·$10^3$. Further bending does not result in significant changes in resistance and maintained at the similar level.

The addition of PVP polymer, which prevents agglomeration, caused a significant deterioration of the resistance to about 7·$10^{10} \Omega$ (Figure 12). The results of the electrical properties measurement are correlated with the surface studies conducted on a scanning electron microscope. The impact of mechanical stress increased. The appearance of micro-cracks after 100 cycles of bending of the substrate increased the resistance to about 1.6·$10^{11} \Omega$. Therefore, registered increases the resistance by more than one order of magnitude.

Table 1: Conversion efficiency of dye-sensitized solar cells with counter electrodes based on platinum and carbon nanotubes with the addition of PEDOT:PSS and PEDOT:PSS/PVP

<table>
<thead>
<tr>
<th>Number of bending cycles</th>
<th>Type of counter electrode</th>
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<tbody>
<tr>
<td></td>
<td>Platinum</td>
</tr>
<tr>
<td>0</td>
<td>4.02 %</td>
</tr>
<tr>
<td>100</td>
<td>2.42 %</td>
</tr>
</tbody>
</table>

Figure 10: SEM images of counter electrode based on carbon nanotubes with addition PEDOT:PSS after 100 bending cycles

Figure 11: Influence of mechanical stress on the resistance of carbon-nanotubes thin films with the addition of PEDOT:PSS deposited on a PET foil

Figure 12: Influence of mechanical stress on the resistance of carbon-nanotubes thin films with the addition of PEDOT:PSS and PVP deposited on a PET foil
The efficiency of dye-sensitized solar cells with different types of counter electrodes is presented in Table 1. These results indicate that the photovoltaic properties of dye-sensitized solar cells after bending is decreased. Platinum is a preferred material for the counter electrode because of its high conductivity and catalytic activity. However, dye-sensitized solar cells based on a platinum counter electrode subjected to the impact of mechanical stress demonstrate the lowest efficiency. This is the result of damage introduced into the platinum thin film deposited by a sputtering method and its delamination from the flexible substrate (Figure 7). These damages have a detrimental influence on the proper working of the solar cell and reduce its properties, which could be a consequence of poorer charge transfer. It can be observed that the carbon-nanotubes counter electrode is more resistant to bending compared to the platinum counter electrode.

4 CONCLUSION

Flexible dye-sensitized solar cells built on elastic substrates have attracted great interest as they are lightweight and can be roll-to-roll printed to accelerate production and reduce costs. The study showed the possibility of replacing the standard platinum counter electrode by carbon nanotubes deposited on the elastic substrate. In the frame of this work, we investigated the influence of mechanical stress arising from the bending of a flexible substrate on the morphology, the resistance of the counter electrode based on carbon nanotubes as well as the electrical properties of dye-sensitized solar cells.

It was found that the bending has a significant influence on the morphology of platinum layer deposited on a PET foil. It was shown that on the platinum surface after bending cracks were formed and in some places the layer was delaminated and broken away from the substrate. The addition of PVP to the counter electrode based on carbon nanomaterials with PEDOT:PSS prevents agglomeration of carbon nanotubes, but after a bending test the resistivity of the prepared layer and electrical properties of produced dye-sensitized solar cells are reduced. The amount of damage and the size of defects in the carbon nanotubes counter electrode is much smaller than in the platinum foil. Moreover, it can be seen that carbon nano-elements reduce the spread of cracks. Mechanical stress slightly effects the resistance of studied carbon nanotubes layers with the addition of PEDOT:PSS. Only the addition of the PVP polymer, which prevents agglomeration, caused a significant deterioration of the resistance as well as the increased influence of mechanical stress. These damages have a detrimental influence on the operation of solar cells and reduce their efficiency.

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5 REFERENCES


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A. DRYGALA et al.: A CARBON-NANOTUBES COUNTER ELECTRODE FOR FLEXIBLE DYE-SENSITIZED SOLAR CELLS


