The Effect of Electrode Immersion Time and Ageing on N719 Dye-Sensitized Solar Cells Performance

Ewelina Krawczak¹, Agata Zdyb¹

¹ Faculty of Environmental Engineering, Lublin University of Technology, Nadbystrzycka 38, 20-618 Lublin, Poland
* Corresponding author’s e-mail: e.krawczak@pollub.pl

ABSTRACT
One of the most promising devices belonging to the third generation of photovoltaic technologies is dye-sensitized solar cell (DSSC). It can be considered as an economic substitute for the first and second generation of solar cells which provides relatively high conversion efficiency at low cost of material and simple manufacturing. This technology is widely developed nowadays thus it can contribute the meeting of the current and future energy demands. However, much work should be done to increase solar-electricity conversion efficiency of DSSC. It is identified that a crucial component which strongly affects the performance of the working dye-sensitized cell is dye sensitizer used to enhance the light harvesting. The adjustment of the amount of the adsorbed dye by a modification of photoelectrode immersion time in dye solution plays a crucial role. The objective of this study was to report the influence of electrode immersion time on dye-sensitized solar cells performance and to evaluate the stability of obtained cells. DSSC assemblies were prepared in the sandwich way with the working area equal to 0.8 cm². The impact of various immersion times in N719 dye solution of the TiO₂ covered photoelectrodes have been investigated. In the study, the process of encapsulation of the cells with sealant gaskets was enhanced which caused the improvement of the stability and tightness of the obtained DSSC devices. The methodological process adopted in this investigation includes measurements of current-voltage (I-V) characteristics performed right after cell preparation, and after 72 hours to evaluate the role of ageing. The characterization of the obtained solar cells was carried out under standard test conditions (STC; temperature 25°C, irradiance 100 mW/cm², air mass AM 1.5). On the basis of I-V curves measurements, characteristic operating parameters of the obtained DSSC assemblies such as open circuit voltage (V_OC), short circuit current (I_SC), and maximum power point (MPP) have been established. The results of this research indicate that the time of electrode immersion in the dye solution affects strongly the DSSC performance. Thus, the control of the stage of the dye adsorption by the TiO₂ layer is vitally important.

Keywords: photovoltaic, PV, dye sensitized solar cells, DSSC, dyes, N719

INTRODUCTION
Continuous development in each field of industry all over the world and thus growing energy demand have a detrimental effect on natural habitat. According to [bp-stats-review-2019-full-report.pdf], in 2019 the strongest growth in energy power demand was noticed in 20-year period time, which was equal to 3.7%. The main resources, which are still used for electricity production, are fossil fuels, such as coal, natural gas, or oil. It is claimed that the energy acquisition process is the main cause of environmental pollution [Louwen et al., 2016]. The fossil fuels combustion causes emission of greenhouse gases, especially CO₂, and thus the climate change. The main problem which communities have to tackle is how to preserve the environment during the energy production process and reduce the level of greenhouse gas emissions into the atmosphere [Höök and Tang, 2013]. It should be mentioned that carbon dioxide emissions increased by 2.0% in 2019 [bp-stats-review-2019-full-report.pdf]. What is more, the Earth’s resources are finite and becoming scarcer every day. This is the result of overusing natural resources regardless of lack of
the supplies replenishment possibilities [bp-stats-review-2019-full-report.pdf]. Therefore, preserving vital resources is a high priority these days and the productive solution for energy production is strongly needed. The exploration of alternative energy sources is crucial and for that reason, the researchers’ attention is focused on this area. In 2019, the renewable power installed all over the World noticed increment by 14.5% which is closed to record increase in 2017 [bp-stats-review-2019-full-report.pdf].

Among all renewables, the Sun is regarded as the most meaningful energy source with huge potential. The above-mentioned factors caused a researchers’ big interest in the photovoltaic (PV) area. Such an advanced development in photovoltaics is noticed not only in the investigations of single solar cells but also plants [Gulkowski et al., 2019; Zidane et al., 2019] and installations of photovoltaic roof tiles [Kurz and Nawrowski, 2017; Wajs et al., 2020]. Nowadays, three main photovoltaic generations can be distinguished in the PV market, whether the first two, based on silicon and thin films, are the most popular ones. Dye-sensitized solar cells are great representatives of photovoltaic devices, which belong to the third generation of photovoltaic solar cells. They are considered as low-cost technology which can be a promising replacement for the commonly used first generation of solar cells [O’Regan and Grätzel, 1991]. Grätzel and G24 Power team obtained the highest efficiency of dye-sensitized solar cells equal to 14.1% [https://www.nrel.gov]. Significant work has been done in DSSC area since 1991, when the outbreak of DSSC was noticed. However, there are still further challenges for researchers: to improve device efficiency, as well as durability and stability because these issues have not been comprehensively studied yet.

Dye-sensitized solar cell is usually composed of: a) working electrode, also called photoanode, modified by photosensitizing; b) counter electrode which is covered with a catalyst, usually platinum; c) liquid state electrolyte with a redox couple (I\(^{-3}/I\(^{-1}\)). The mesoporous photoanode is a key component that normally consists of transparent conductive oxide (TCO) layer partly covered with nanocrystalline titanium dioxide (TiO\(_{2}\)) thin layer. The TiO\(_{2}\) is used in DSSC because of high possibility of the dye adsorption and appropriate energy level [Quintana et al., 2007]. TCO glass substrate is usually made of indium-doped tin oxide (ITO) [Shikoh et al., 2017; Hossain et al., 2018] or fluorine-doped tin oxide (FTO) [Subalakshmi and Senthilselvan, 2018]. However, nowadays the FTO glasses are more common to use due to their higher temperature resistance in comparison with ITO. As the temperature rises, the electrical properties of ITO become deteriorated. Among different oxide-based materials, ZnO enriched with trivalent dopants, such as Al [Zdyb et al., 2018; 2016], Ga [Gong et al., 2014; Parthiban et al., 2015] and B [Zhang et al., 2016; Ueno et al., 2013] is the valuable replacement to ITO and FTO since it is able to offer wide band gap, good optical (high visible transmittance) and electrical properties (low resistivity) simultaneously. The efficiency of dye-sensitized solar cell highly depends on the quality of the photoanode due to determination of electron transfer, capability of light harvesting, optimal cooperation between TCO glass and electrolyte [Kundu et al., 2017; Galliano et al., 2018; J. Gong et al., 2017].

The counter electrode (CE) is also based on ITO or FTO transparent conductive oxides-covered glass substrates. The main role of counter electrode is dye regeneration by catalyzation of reduction of I\(^{-3}\) to I\(^{-1}\) ions and collecting the electrons from the external circuit [Grätzel, 2005]. The liquid state electrolyte with a redox couple (I\(^{-3}/I\(^{-1}\)) is commonly used due to assurance of high electron transfer and large recombination resistance [Teuscher et al., 2014]. The role which photosensitizer plays in dye-sensitized solar cell assembly is also very important. Photosensitizer should be characterized by a wide absorption spectrum (from the visible to near infrared region) that extend the absorption spectrum of TiO\(_{2}\) layer, and provide efficient electron injection into the working electrode. When incident light reach the dye-sensitized solar cells surface, the electrons of the sensitizer adsorbed onto surface of TiO\(_{2}\) become exited and then they are transferred into the conduction band of TiO\(_{2}\) [Krawczyk et al., 2018]. The electrons are infused into the conductive layer of the transparent oxide material, ITO or FTO, and then they reach the counter electrode through the external circuit. To complete the working cycle, the oxidized dye is regenerated by the electrolyte with electrons that are collected at counter electrode. In order to regenerate the electrolyte, the reduction reaction occurs at counter electrode which leads to restoring the initial state [Nazeeruddin et al., 2011]. Taking into account all the factors mentioned above, in order to improve the
power conversion efficiency (PCE) of dye-sensitized solar cells, the research is conducted in the field of photoelectrodes [Unal et al., 2020; Peng and Xu, 2020], electrolytes [Önen et al., 2019; Chowdhury et al., 2020], counter electrodes [Rahman et al., 2019; Zalas and Jelak, 2020] and photosensitizers. The photosensitizers can be divided into two main groups: metal-free dyes and metal complex dyes, based mainly on ruthenium [Karim et al., 2019]. Nowadays, the natural dyes, such as pigments extracted from flowers, leaves, and fruits of some plants, are under strong development [Kabir et al., 2019; Krawczak and Zdyb, 2019; Singh and Koiry, 2018; Zdyb and Krawczyk, 2016], but still the DSSC based on ruthenium complexes are characterized by the highest working parameters. Many photosensitizers based on Ru element were developed, such as N3 (“red” dye), N749 (“black” dye), and N719. However, there are still issues, such as stability, tightness, and influence the immersion time on PCE, which must be improved.

In this work, N719 dye was applied in DSSC as a sensitizer and a relation was established between the concentration of the dye, the time of electrode dipping in the dye solution, and DSSC performance. The effect of ageing of the cells was also studied in terms of its influence on the DSSC working parameters. The performed series of experiments allowed evaluating of sealing procedure that was worked out in order to obtain durable cell structure.

**METHODOLOGY**

**Preparation of TiO$_2$ photoanode**

The TiO$_2$ paste was prepared following the procedure described in [Ito et al., 2007]. Mesoporous TiO$_2$ layers were prepared by the use of TiO$_2$ paste onto fluorine-doped tin oxide-covered glasses substrates. The FTO glasses with a size of 2×2.5 cm, which were purchased from Greatcell Solar, are characterized by 18 Ω/sq sheet resistance. Prior to the deposition process, the substrates were chemically cleaned in acetone and ethanol, and dried in nitrogen gas flow. Thin TiO$_2$ layers were formed firstly by the use of doctor blade technique in the rectangular shape of 0.8 cm$^2$ area ($A$) and then the spin-coating. Following the paste deposition process, the layers were sintered in the temperature up to 450° in a few-steps process in order to obtain layers crystallization and enhance particles interconnectivity. The sintering process was carried out in the programmable high-temperature titan hotplate from Greatcell company with a possibility to control the ramp times, constant times, and temperature. The samples were cooled down naturally and then were moved directly to N719 dye solution.

**Assembling of dye-sensitized solar cells**

The dye-sensitized solar cells were prepared based on different concentrations of the dye and various immersion times of photoanodes. The N719 dye solutions were prepared with the use of 99.8 % ethanol and N719 (Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)) dye from Sigma-Aldrich. Dye solutions were ultrasonically mixed for 10 minutes in order to improve the solubility of dye particles. The following concentrations of dye in absolute ethanol were prepared: 0.25 mM, 0.5 mM, and 1 mM. Prepared TiO$_2$ photoanodes were immersed in the N719 dye solutions and remained there for 1 hour, 2 hours, or 24 hours in complete darkness. After the immersion process, the samples were rinsed with ethanol (99.8%) to remove additional dye particles from TiO$_2$ thin layers and dried at room temperature (RT=25°C). In order to assemble the solar cells, the prefabricated Pt-coated counter electrodes, purchased from Greatcell Solar, were used. Encapsulation of the cells was realised by using the low-temperature thermoplastic gasket sealant (from Dye Sol) with a 0.8 cm$^2$ cut space by applying temperature and pressure. The solar cells were assembled in sandwich way then heated up to 125° in order to encapsulate the whole structures properly and finally cooled down naturally. High performance EL- HPE electrolyte by Greatcell Solar was injected by the drilled hole in the back of counter electrode. In order to enhance charge collection, the contacts of silver paste were deposited. The steps required to assemble the dye-sensitized solar cells are presented in Figure 1.

**Characterization of dye-sensitized solar cells**

The current-voltage ($I$-$V$) characteristics of the obtained dye-sensitized solar cells were measured by the use of SUN 3000 Abet Technologies solar simulator with a xenon lamp. The investigation was carried out under the light intensity ($G$)
of 100 mW/cm² which was calibrated with the use of standard Si solar cells. Additional parameters were: temperature equal to 25°C and AM 1.5. In order to measure the generated photocurrent, the Keithley Instruments, model 2440, digital source meter was used. The measurements were carried out directly after assembling DSSC device and 72 hours later in order to evaluate the ageing effect. The working parameters of the DSSC, such as $I_{sc}$ – short circuit current, $V_{oc}$ – open-circuit voltage, $I_{MPP}$ and $V_{MPP}$ – maximum power point current and voltage respectively, $MPP$ – maximum power point, as well as the value of fill factor ($FF$) and efficiency were calculated with the use of Matlab software. The efficiency of the achieved DSSCs was calculated on the basis of equation (1).

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{l_{\text{max}} \cdot v_{\text{max}}}{P_{\text{in}}} = \frac{l_{\text{SC}} \cdot V_{\text{OC}} \cdot FF}{G \cdot \alpha} \quad [\text{–}]$$

(1)

where: $P_{\text{max}}$ is maximum power output and $P_{\text{in}}$ is incoming light power. As can be seen from equation (1), the value of maximum power is defined as a product of the maximum current ($I_{\text{max}}$) and maximum voltage ($V_{\text{max}}$) which can be obtained by the solar cell. Nonetheless, these two values are not generally used for the comparison of solar cells, because they are not directly visible in the $I-V$ curves. Fill factor ($FF$) is determined by the relation between the maximum power ($P_{MPP}$) that the cell can produce under given operating conditions, and the product of open-circuit voltage and short-circuit current, Eq (2). This factor indicates the quality of the solar cell, the closer it is to 1, the more power it can provide.

$$FF = \frac{P_{\text{MPP}}}{l_{\text{SC}} \cdot V_{\text{OC}}} \quad [\text{–}]$$

(2)

RESULTS AND DISCUSSION

Three sets of dye-sensitized solar cells were carefully made according to the precise description presented in the previous section. In order to find optimal technological parameters related to immersion time and the concentration of dye solution, a great number of experiments was conducted. Each measurement of $I-V$ characteristic was performed for freshly assembled cells and subsequently after 72 h (three days) to evaluate the stability of the cells and the changes in their electrical parameters. The parameters of each experiment series are shown in Table 1.

Figures 2–4 present the exemplary characteristics of the cells that exhibit the best achieved photovoltaic parameters. Figure 2 depicts $I-V$ characteristics obtained for dye-sensitized solar

<table>
<thead>
<tr>
<th>No</th>
<th>Dye</th>
<th>Dye concentration (mM)</th>
<th>Dipping time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N719</td>
<td>0.25</td>
<td>1 h, 2 h, 24 h</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.50</td>
<td>1 h, 2 h, 24 h</td>
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<td>3</td>
<td></td>
<td>1.00</td>
<td>1 h, 2 h, 24 h</td>
</tr>
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</table>
cells which were immered for 24 hours in N719 dye solution with concentration of 0.25 mM, measured directly after DSSC preparation and 72 hours later.

As can be seen from Figure 2, at the outset, the value of the short-circuit current was 8.59 mA, whereas the open circuit voltage was equal to 693.07 mV. The short circuit current density $I_{sc}$ value of the freshly made DSSC cell was equal to 10.74 mA/cm$^2$, $V_{MPP}$ and $I_{MPP}$ were 6.72 mA and 469.72 mV respectively and thus the maximum power was 3.16 mW. After 72 hours, the increase in all working parameters can be observed. Increase in $V_{oc}$ (712.54 mV), $I_{sc}$ (11.49 mA/cm$^2$), $V_{MPP}$ (474.4 mV), $I_{MPP}$ (7.29 mA) was noticed. What is more, the 10% change in $I_{sc}$ was distinguished (from 8.59 to 9.19 mA). The efficiency of the DSSC changed from 3.94 % to 4.33% and the increase in maximum power value to 3.46 mW was also observed. The value of the $FF$ did not change significantly, prior ageing it was 52.97%, whereas at the end of the process it was equal to 52.85%.

The dye-sensitized solar cells obtained by dipping the electrode in 0.5 mM N719-dye solution for 2 hours also showed an increase of the working parameters. The current-voltage curves are shown in Figure 3. It is interesting to notice that the samples obtained from these experiments were characterized by higher outset values than obtained by 24 hour-immersion but in 0.25 mM dye solution (Figure 2). However, the smaller change is visible in measurements made directly after DSSC preparation and after 72 hours in comparison with the previous ones.

The $I_{sc}$ value changed from 9.76 mA to 9.97 mA, which means 2% of the variation. Thus, the short-circuit current density also changed in the range of 12.21 mA/cm$^2$ – 12.47 mA/cm$^2$. The $V_{oc}$ increased from 708.5 mV to 723.98 mV and so the values of $I_{MPP}$ (from 7.82 to 8.10 mA), $V_{MPP}$ (from 465.00 to 479.11 mV). The 7% change was observed in maximum power point value which at the beginning was equal to 3.64 mW and after 72 hours was 3.88 mW. The gentle variations were also noticed in $FF$ that changed from 52.58% to 53.78% and $\eta$ which was equal to 4.55% at the beginning and later to 4.85%. All these measurements show the good stability of the obtained dye-sensitized solar cell.

In Figure 4, the $I$-$V$ characteristics are shown for the immersion in 1 mM dye solution which took 1 hour time. In these experiments, the positive change also can be observed after 72 hours in the prepared dye-sensitized solar cells. Initially obtained values of the majority of the parameters were lower than after ageing process. The $V_{oc}$ value increased from 691.4 mV to 713.31 mV, $I_{MPP}$ value changed from 7.37 mA to 7.49 mA, as well as $V_{MPP}$ value rose from 455.59 mV to 469.7 mV.

Thus, the maximum power values noticed 5% increase, from 3.36 mW to 3.52 mW, the $FF$ also changed from 49.15% to 50.16%. What is more, the variation in the working parameters reflected in the variation of the $\eta$ in which 20% improvement was distinguished (4.19% to 5.03%).

The working parameters of all prepared sets of dye-sensitized solar cells are summarized in Table 2 in which short circuit current density ($I_{sc}$), open-circuit voltage ($V_{oc}$), maximum power point

![Figure 2. I-V characteristics for N719 dye-based DSSC performed right after cell preparation, and after 72 h, obtained for immersion time equal to 24 h and 0.25 mM dye solution.](image)

![Figure 3. I-V characteristics for N719 dye-based DSSC performed right after cell preparation, and after 72 h, obtained for immersion time equal to 2 h and 0.5 mM dye solution.](image)
current ($I_{mp}$) maximum power point voltage ($V_{mp}$) maximum power (MPP), fill factor (FF) and efficiency ($\eta$) are included. The table presents results of measurements that were conducted onto freshly made DSSC and after 72-hour aging process.

The maximum efficiency of 4–5% can be achieved when the proper amount of the dye is adsorbed on TiO$_2$ electrode which means that the combination of dye concentration and time of soaking the electrode in dye solution is optimal. The results show that dipping in dye solution of low concentration (e.g. 0.25 mM) requires longer time of electrode immersion in the solution (e.g. 24 h). The set of samples no. 3 achieved the highest working parameters from 0.25 mM-group of the tested cells. The 24-hour immersion allowed to obtain 142% higher $J_{sc}$ value compared to sample no. 1 and 10% improvement compared to sample no. 2. The same trend is visible in $\eta$ value. The opposite relation also works, thus higher dye concentration needs to be accompanied by shorter dipping time. This can be shown on the basis of the set of samples no. 5 and 7. The best performance obtained the sample immersed by 2 hours (sample no. 5) which results in 20% improvement compared to sample no. 2. The same trend is visible in $\eta$ value. The opposite relation also works, thus higher dye concentration needs to be accompanied by shorter dipping time. This can be shown on the basis of the set of samples no. 5 and 7. The best efficiency values are achieved for the following combinations of concentration and time: 0.25 mM and 24h, 0.5 mM and 2h, 1 mM, and 1h (Table 2). The experimental results also indicate that the higher dye concentrations (0.5 mM and 1 mM) are preferable. Measurements performed 72 h after the preparation of the cells provide better results than performed right after the assembly of the cells. This observation can be

Table 2. Characteristic parameters of dye-sensitized solar cells differing by dye concentration and time of dipping in the N719 dye solution. Ageing was evaluated by comparison of the measurements performed right after cell preparation – row A, and later, after 72 h – row B in the third column.

<table>
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<th>No.</th>
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<th>Ageing</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$I_{sc}$ [mA]</th>
<th>$V_{oc}$ [mV]</th>
<th>$I_{mp}$ [mA]</th>
<th>$V_{mp}$ [mV]</th>
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<th>FF [%]</th>
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explained with penetration of electrolyte which requires some time to fill the mesoporous structure of TiO₂ layer. It is interesting to notice that the improvement in working parameters is legible and it is found that ageing effect shows a positive influence on working parameters. Even 20% improvement of parameters can be observed after 72 hours (e.g. efficiency of sample no. 7 changed from 4.19% to 5.03%). The loss of performance occurring after 72 hours in sample no. 1 can be explained by progressive loss of electrolyte that resulted in improper operation of the cell.

CONCLUSIONS

Dye cells sensitized with N719 dye were prepared and sealed according to the procedure that assure their the proper operation. The vast majority of the cells were stable during the measurements and no leakage of the electrolyte was observed for minimum a few days. The results show that the increase of dye solution concentration has to be accompanied by the decrease of dipping time of the TiO₂ electrode in order to achieve the finest performance parameters. The cell prepared with the electrode immersed for 1 h in 1mM dye solution exhibited the highest efficiency of 5% after ageing for 72 h. The beneficial influence of ageing was observed in the presented results which suggest that liquid electrolyte needs some time to penetrate the pores in TiO₂ structure and create the interface enabling electrons to transfer in order to regenerate the dye.

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REFERENCES