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Optimization and characterization of TiO₂-based solar cell design using diverse plant pigments



R.A. Voloshin ^a, V.S. Bedbenov ^a, D.A. Gabrielyan ^a, N.G. Brady ^b, V.D. Kreslavski ^{a,c}, S.K. Zharmukhamedov ^c, M.V. Rodionova ^a, B.D. Bruce ^{b,d,**}, S.I. Allakhverdiev ^{a,c,e,f,*}

^a Controlled Photobiosynthesis Laboratory, Institute of Plant Physiology, Russian Academy of Sciences, Botanicheskaya Street 35, Moscow 127276, Russia

^b Department of Biochemistry, Cellular & Molecular Biology, University of Tennessee at Knoxville, 125 Austin Peay Bldg., Knoxville, TN 37996, USA

^c Institute of Basic Biological Problems, Russian Academy of Sciences, Pushchino, Moscow Region 142290, Russia ^d Department of Microbiology, University of Tennessee at Knoxville, 125 Austin Peay Bldg., Knoxville, TN 37996, USA

^e Bionanotechnology Laboratory, Institute of Molecular Biology and Biotechnology, Azerbaijan National Academy of Sciences, Baku, Azerbaijan

^f Department of Plant Physiology, Faculty of Biology, M.V. Lomonosov Moscow State University, Leninskie Gory 1-12, Moscow 119991, Russia

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ABSTRACT

The design of electrochemical solar cells (SCs), including those composed of biological pigments is an actively developing direction of obtaining alternative energy. SCs were studied under different temperatures, light intensities and spectral conditions. Furthermore, to understand processes occurring in the SCs, investigations characterizing the efficiency and stability with regard to environmental factors are also required. For this aim, novel instrumentation for the investigation of environmental effects on photocurrent generated by SCs has been designed and constructed. The system can be a model, which reflects conditions required for effective and stable functioning of the solar cells. Preliminary results are shown for two types of solar cells with two photosensitizers: thylakoid membrane preparations and anthocyanin-enriched raspberry extracts. It was shown that electrogenic activity decreased by a half at 40 °C and returned back to the initial value under gradual cooling. Maximum current obtained from the thylakoid-based SC was 0.46 μ A, while maximum current generated by the anthocyanin-based SC was 1.75 μ A. The goal of this investigation is to find new ways to increase efficiency and stability of bio-

Abbreviations: Asc-Na, sodium ascorbate; Chl, chlorophyll; DC, direct current; DCPIP, 2,6-dichlorphenolindophenol; DS-PEC, dyesensitized photoelectrochemical cells; DSSC, dye-sensitized solar cell; EQE, external quantum efficiency; LED, light-emitting diode; SC, solar cell; TiO₂, titanium dioxide; UV, ultraviolet.

^{*} Corresponding author. Controlled Photobiosynthesis Laboratory, Institute of Plant Physiology, Russian Academy of Sciences, Botanicheskaya Street 35, Moscow 127276, Russia.

^{**} Corresponding author. Department of Biochemistry, University of Tennessee at Knoxville, 125 Austin Peay Bldg., Knoxville, TN 37996, USA.

E-mail addresses: bbruce@utk.edu (B.D. Bruce), suleyman.allakhverdiev@gmail.com (S.I. Allakhverdiev). http://dx.doi.org/10.1016/j.ijhydene.2016.11.148

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based SCs. In future, this measuring system can be used for investigation of solar cells based on long-wave forms of chlorophylls (Chls d and f) and components of the photosynthetic apparatus comprising these chlorophylls.

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Introduction

Currently, many studies focused on the development and creation of non-conventional solar cells has been carried out in different parts of the world. This thrust has primarily been driven by the high cost of production of conventional silicon based solar cells [1,2]. One of the most promising alternatives to silicon solar cells is the dye-sensitized solar cell (DSSC) commonly referred to as the Gratzel cell [3,4]. Moving forward, these devices could compete with silicon solar cells due to the use of cheaper components and efficiency approaching comparable levels. Currently, the best laboratory samples of DSSCs have about 11% efficiency while the efficiency of commercial silicon solar cells is less than 20% [2,5].

Typical DSSCs consist of three parts: photoanode, electrolyte and cathode (Fig. 1) [6]. Both electrodes are made from a specific glass that has a transparent conductive layer coating on one side. The anode is covered by a film of mesoporous, semiconducting nanoparticle material. This mesoporous material has a large specific surface area upon which sensitizer material (a dye) is absorbed. The actual surface area of 10 μ m semiconductor layer with 50% porosity is about thousand times greater than that of an unstructured layer [7]. Titanium dioxide is the most commonly used semiconductor [7]. Polypyridyl complexes of ruthenium are typical sensitizers for DSSC [8-11]. There is an electrolyte between the electrodes to facilitate electron transfer from the cathode to the anode via a redox couple. Reactions occurring in the DSSC are divided into the forward reactions and reverse reactions [10,12]. Each of these reactions is characterized by reaction time or half-life [14,13]. Forward reactions include: light harvesting by sensitizers, electron transfer from sensitizer to conduction band of semiconductor, electron diffusion through semiconductor to the electrode, regeneration of oxidized sensitizer molecules by reduced species of electrolyte, the diffusion of oxidized species in the electrolyte to the cathode where reduction occurs, and conversely, the diffusion of reduced electrolyte species to the cathode [10]. Reverse reactions include: fluorescence or nonradiative relaxation of excited states of the sensitizer, reduction of oxidized electrolyte species at the anode by electron from conduction band of semiconductor and the reduction of the oxidized sensitizer by electron from conduction band of semiconductor [10,12]. In the ideal DSSC, maximum rates of forward reactions are achieved and reverse reactions do not occur. The higher is the rate of forward reactions compared to reverse reactions, the more effective is the solar cell.

Electron transferring through the electrolyte (a limiting step of the forward reactions) and reverse reactions of recombination are temperature-dependent. This suggests a complex relationship between solar cell efficiency and the



Fig. 1 – Structure and working principles of DSSC. (1) – glass plate, (2) – transparent conductive covering, (3) – mesoporous semiconductor layer, (4) – molecules (macromolecular complexes) of sensitizers, Ox. and Red. – oxidized and reduced species of electrolyte, respectively, $h_{\rm V}$ – incident light quantum; $h_{\rm Vf}$ – fluorescence quantum; Heat – heat dissipation of excited state. Solid arrows indicate forward reactions; dotted arrows indicate reverse reactions.

temperature. Also, photocurrent is proportional to the light intensity [10].

Ruthenium-based sensitizers have some disadvantages, including:

- 1) High cost, as this compound is one of the most expensive components of the DSSC [8,15].
- Toxicity, it is potentially harmful as it includes a heavy metal [8].
- Charge recombination, fast reverse reaction of electron transfer from TiO₂ to sensitizer limits the DSSC efficiency [10].

Biological pigments or pigment–protein complexes have some advantages in comparison with synthetic rutheniumbased dyes: simplicity, low cost and environmentally benign manufacturing capability [8,15,16].

Anthocyanins and components of the photosynthetic apparatus are of the most interest for being used as natural sensitizers. Anthocyanins from berries and flowers have proven to be easily accessible and simple sensitizers [16]. Because of this, they are often used for demonstrative purposes in education [17]. Components of the photosynthetic apparatus, such as isolated complexes of photosystem I, or thylakoid membrane preparations, are of interest because they provide very effective charge separation [18,19]. They are complicated complexes which include a large cluster of antenna pigments and a complex system of primary electron carriers. As a result, there is a system in which charge separation occurs with almost 100% probability following excitation of the reaction center by light [18]. Thus, the reverse reaction of electron transfer from TiO₂ to the chlorophyll sensitizer molecule is highly improbable. However, solar cells based on these complexes have low efficiency for the following reasons:

- 1) Small optical density of such cells.
- 2) Weak absorption in green, far-red and near ultraviolet parts of spectrum [20,21].
- 3) Low stability and high sensitivity to the changes of the environment of isolated photosynthetic complexes [20].

The first problem can be solved by creation of TiO_2 layer with larger pore size. The second problem can be solved by several ways, such as: the use of specifically engineered complexes, implementation of complexes with special chlorophyll species capable of absorbing far-red light [18,22] or the use of hybrid pigment—protein complexes with quantum dots [23]. The third constraint can be mitigated by using special stabilizing agents or chemical linkers [18].

Today, the development of bio-based DSSCs is steady, however considerable room for improvement and optimization of these systems still remains. The one of such areas of interest with regard to optimization is photocurrent generation of SCs under varying light intensity and/or temperature. Photocurrent generation is non-linear across a large range of temperatures [10]. In addition, isolated components of the photosynthetic apparatus are highly susceptible to variations in environmental conditions [20]. In the literature, a multitude of works has been conducted to investigate the influence of temperature, light intensity and spectral properties on the components of the photosynthetic apparatus *in vivo* and *in vitro* [24–26]. Studies concerning the impact of these factors on the efficiency of non-bio-based solar cells can also be found [10,27,28]. In accordance with the data received by Peng and Berberoglu (2013), efficiency of ruthenium-based DSSC increases with increasing temperature in the range of $5^{\circ}C-15^{\circ}C$ and decreases with temperature in the range of $15^{\circ}C-50^{\circ}C$ [10]. This has been explained by the following: in the first temperature range, the rate of the forward reaction increases as the rate of ionic diffusion in the electrolyte is higher than the rate of reverse reaction of recombination; but in the second range, the opposite is observed. Also, it has been shown that the photocurrent exhibits a linear relationship to the light intensity [10].

However, for bio-based DSSCs photocurrent dependence on temperature, light intensity and wavelength is yet to be elucidated. Further characterization of these parameters is needed, as dye degradation can be observed under high temperature conditions in DSSCs. Then, the effects of temperature dependence of these systems have previously not been taken into account. Information pertaining to the behavior of bio-based DSSCs under different temperatures, light intensities and wavelength is useful for development and investigation of bio-based SCs. The creation of a system to measure the photocurrent generation of DSSCs under different temperature and light conditions can help to gain insight into the significance of these parameters as they pertain to overall system performance.

It is also worth paying attention to one more thing. Hydrogen is very attractive environmental fuel. It can be obphototained by non-expensive dye-sensitized electrochemical cells (DS-PECs) [29]. DS-PEC is fuel cell for hydrogen production which operates on the principle of the DSSC. It also has nanostructured TiO₂ sensitized by dye on the one of the electrodes. The difference lies in the following. Cathode of such cell covered by layer of water oxidation catalysts. And anode dye connects with hydrogen evolving catalyst through some nanowires. After light quantum adsorption, electron from dye goes through the nanowire and activates hydrogen evolving catalyst. DS-PEC based on the biological photosystem with hydrogenase is very attractive system. It is clear that the rate of hydrogen evolution in these PECs depends on the temperature, light intensity and spectral composition.

Description of the experimental set-up

The laboratory set-up for the investigation of certain environmental conditions and measurement of photocurrent output generated by the SCs has been designed and constructed in the Laboratory of Controlled Photobiosynthesis in Institute of Plant Physiology (Russian Academy of Sciences). Pictures of the set-up are shown in Fig. 2. The above experimental design allows for the measurement of current under conditions of varied light intensity, wavelength and temperature of the SC. The laboratory set-up scheme is shown in Fig. 3. Variation of light intensity is achieved by using neutral optical filters (6) with different optical density, which have



Fig. 2 – Pictures of the laboratory testing set-up. A. General view of the laboratory set-up using the thermostat as a heating and cooling device and the analog galvanometer to measure current; B. General view of the laboratory set-up using a heating element and tap water as a coolant; C. thermostatic chamber; D. Laboratory solar cell with thylakoids. (1) – light source; (2) – thermostatic chamber with SC; (3) – temperature regulator module; (4) – galvanometer; (5) – thermostat; (6) – module with an analog to digital converter and output data to a computer; (7) – thermocouple; (8) – heater; (9) – coolant feed tube; (10) – laboratory solar cell.



Fig. 3 – The laboratory set-up scheme. (1) – Stand;
(2) – movable platform; (3) – movable platform locker;
(4) – support platform; (5) – light source; (6) – optical filter;
(7) – focusing lens; (8) – SC; (9) – radiator of thermostatic chamber; (10) – thermostatic chamber; (11) – input coolant tube; (12) – output coolant tube; (13) – temperature regulator module; (14) – thermocouple 1 (radiator); (15) – thermocouple 2 (chamber); (16) – heater; (17) – DC output current signal meter; (18) – computer (control and analysis of results).

minor changes at different wavelengths within visible range. Optical filters are placed between the light source (5) and lens (7) (or the object of study in the absence of the lens). Additionally, the use of light sources with different parameters (power, spectral composition of the light, etc.) allows for the observation of SC current dependence of the output current signal (8) on the intensity of light in various ranges.

Changing the wavelength of light is possible by installing spectrally distinct light filters. Varying the temperature of SCs was carried out using a special chamber (10) in which coolant is circulating at a predetermined and controlled temperature. The slim housing of the cell fits tightly to the surface of the thermostatic chamber radiator (9) that provides stationary heat transfer and maintains the cell at a temperature equal to that of the radiator surface.

The constancy of the flow temperature can be achieved by two ways. The first way is achieved by connecting the input (11) and output (12) tubes of the chamber to the thermostat, which is set on the desired temperature value. The thermostat MULTITEMP II Thermostatic Circulator brand LKB Bromma is used in this work, at an operating temperature range from 0 to 90 °C. The second way to control temperature is by means of a heating element, controlled by the temperature regulator module. The dual channel regulator (13) with an accuracy of 0.25/0.5 °C is produced by OVEN Company (Russian Federation), and used to determine the temperature of the radiator surface for controlling the heating element (16). Platinum-platinum (14) and chromel-alumel (15) thermocouples are connected to the temperature regulator module. Thermocouple 1 registers the temperature of the coolant in a thermostatic chamber near a radiator. Thermocouple 2 registers the temperature of the radiator surface on which the cell is installed. The error of signal measurement from the thermocouples (13) is $\pm 0.5\%$.

The cartridge-type heating element (16) is connected to the temperature regulator module and has a power of 80 W. It is automatically switched on/off depending on the boundary temperature values set in the module, and the coolant temperature in the chamber (10) is measured by the thermocouple (15).

LED G9-01 lamp used as the light source has the following parameters: power 2.2 W and 3000 K light chromaticity.

Optical colored glasses produced at Leningrad Optical Mechanical Association are used to obtain light of different spectral compositions. The lens (7) is used to focus the light from the source (5), wherein the movable platform (2) is fixed with the locker (3) at a distance from the working surface of the thermostatic chamber, so that the light spot covers the entire working area where SC is installed.

As a device for measuring of the DC output (15), the following two devices have been used: A highly sensitive portable multi-range galvanometer (GOERZ, Germany) with light pointer, and a Galvanometer, which provides current measurements in the range from 0.5 μ A to 1 mA. The accuracy of current measurements is $\pm 1\%$ of full scale on all ranges of measurement. The temperature regulator module, the light source and the galvanometer are powered by main voltage of 220 V. The module E14-440 L-card, which is a multichannel analog-to-digital converter capable of exporting the data to the computer, is used as another DC current measurement device. Software package Power Graph 3.0 is used for data analysis.

A LI-COR LI-189 photometer is used for light intensity measurements. Neutral density optical filters used to change the spectral characteristics of the light and intensity are described in Ref. [30]. Primary analyses consisting of two types of solar cells were conducted by means of this laboratory set-up. Raspberry extract was used as a sensitizer in the cells of the first type. Thylakoid membranes isolated from pea leaves were used as the photosensitizer in solar cells of the second type.

Materials and methods

Materials

Frozen berries of red or European raspberry (Rubus idaeus) and fresh leaves of dwarf pea seedlings (Pisum sativum, Laxton Progress No. 9) were used as sources of photosensitizers. Glycine—betaine (Sigma Aldrich, USA) was used to increase stability of thylakoid membrane preparations. Sodium ascorbate and 2,6-dichlorphenolindophenol (Sigma Aldrich, USA) were used for increasing of rate of oxidized sensitizer reduction. Polished Float Glass plates with transparent conductive covering of indium tin oxide on the polished surface with the SiO₂ passivated, Rs = 9–15 Ω , cut edges, 25 × 25 × 0.7 mm (Delta Technologies, Loveland, CO). Paste of TiO₂ and iodinebased electrolyte were purchased from Solaronix Company, Switzerland, and were used in both types of cells.

Methods

Preparation of sensitizer

Thawed berries were crushed by means of mortar and pestle for making anthocyanin-based sensitizer. The resulting mixture was filtered through cheesecloth to remove solid material. Thylakoids were isolated from pea leaves and chlorophyll concentration was measured in resulting mixture according to known procedures [31]. Sodium ascorbate, DCPIP and glycine-betaine were added to this preparation. The resulting solution contained 2.9 \pm 0.15 mg of chlorophyll per ml, 0.5 M glycine-betaine, 50 mM Asc-Na and 1.25 mM DCPIP.

Cell preparation

TiO₂ paste was applied to the conductive side of the glass electrodes using a doctor blading method. The thickness of the layer was $38 \pm 7 \mu m$. The anodes were then sintered on a programmable hotplate (IKA C-MAG HP 7) at 500 °C for 15 min. The uniformity of the TiO₂ surface can be seen in Fig. 4. After the cooling of sintering anode, sensitizer was



Fig. 4 – SEM of the TiO₂ nanoparticles. The TiO₂ has been doctor bladed on ITO polished glass slides and sintered at 375 °C for 90 min. Following sintering the surface was imaged using our Auriga FIB SEM operating at 3 KV and 5.5 \times 10⁻⁶ mbar vacuum. A) is shown at 17.4 K X magnification. B) Is shown at 161 K X magnification. C) Is shown at 333 K X magnification.

added. In the case of anthocyanin-based SCs, this electrode was soaked in raspberry extract for about 24 h. For thylakoidbased solar cell, thylakoid preparation was deposited above TiO₂ layer and it was soaking during about 16 h. Soaking was performed under 4 °C. Lastly, non-absorbed residues were removed from the anodes with an ethanol wash. Another glass plate without TiO₂ layer was then placed on the top of this anode. These plates were conjugated by double sided tape. A small portion of each electrode was left uncovered for electrical contacts. Electrical contact was ensured by wires that were attached to glass electrodes by conductive glue. 10 μ l of electrolyte was added between the electrodes, permeating between the glass pieces via capillary action. It is known that TiO2 absorbs light in UV and violet region of spectrum [32]. However, the value of photocurrent generated by DSSCs without sensitizer was comparable with noise. Activity of primary photosynthetic reaction centers was proved by fluorescence analysis. The maximum photochemical quantum yield in thylakoid preparations was about 0.62 ± 0.05. IMAG-PAM mini (Walz, Germany) was used for fluorescence measurements.

Experiment parameters

Temperature effect

We increased temperature stepwise while the current was measured continuously. After three or four steps, we decreased temperature to near initial level. Therefore, there were several temperature values which varied slowly throughout a 4–6 min period. Following this interval, temperature was changed to next stationary temperature state. Transition time between two stationary temperature states was about 2–3 min. In this experiment, light intensity in solar cell exposed to the white light was I = 60 ± 2 quantum µmol m⁻² s⁻¹. For anthocyanin-based DSSC, we regulated temperature as follows:

 $21.4 \pm 0.1 \rightarrow 27.8 \pm 0.1 \rightarrow 32.5 \pm 0.1 \rightarrow 39.5 \pm 0.1 \rightarrow 21.4 \pm 0.1 \,^{\circ}\text{C}.$

For thylakoid-based DSSCs, we regulated temperature as follows:

 $23.6 \pm 0.1 \rightarrow 29.5 \pm 0.5 \rightarrow 39.0 \pm 0.3 \rightarrow 22.5 \pm 0.1 \,^{\circ}\text{C}.$

Light modulation

First, the impact of white light intensity on the photocurrent was investigated. We altered light intensity during the continuously measuring of the current by adding or removing neutral density light filters. Before the measurement, DSSCs were adapted in the dark for 10 min. Light intensity was altered in a stepwise fashion as follows: $20.6 \pm 0.2 \rightarrow 59.5 \pm 0.7 \rightarrow 95.6 \pm 1.1$ quantum µmol m⁻² s⁻¹, for both cell types. The cell was exposed to each of these light intensities for 3 min. DSSCs were maintained under constant temperature 26 ± 1 °C in the experiment. In this investigation, we presented typical results for both types of DSSC. Then photocurrent was measured under incident light of different compositions and the same light intensity of 13.0 ± 1.1 quantum µmol m⁻² s⁻¹ and temperature of 26 ± 1 °C. We used light filters of three colors: blue, green and red. Intensity values were equalized by neutral density light filters.

Values of photocurrent were recorded after the observed current value was stabilized.

IPCE or external quantum efficiency determination

Measurements were made using an Oriel Quantum Efficiency Measurement System, from Oriel Instruments, a Newport Corporation brand. The raspberry juice was extracted using previously outlined methods, thawed berries crushed with a mortar and pestle and filtered through Miracloth (Calbiochem). DSSCs were measured at 10 nm intervals in wavelength, from a range of 375 nm-675 nm. The external quantum efficiency at each step was determined directly, by monitoring generated photocurrent as a function of the wavelength of light irradiating the cell. The DSSCs were made in duplicate, and were found to be within 10% difference in external quantum efficiency. Error bars represent standard deviation across 9 scans of the DSSC. All IPCE curves were measured at room temperature. To confirm that none of the photocurrent was derived from the photo-activity of the TiO_2 , a similar IPCE curve was performed on identical solar cells prior to the addition of the pigments.

Absorbance measurement

Absorption spectra of fresh organic raspberry pigment was obtained using a Thermo Scientific Evolution 300 UV–vis spectrophotometer. The extracted pigment was diluted 20 fold prior to analysis, and scanned in triplicate. The results of the three scans showed a variance of less than 1%, and max absorbance (~0.8 AU) was measured at 515 nm.

Results

The use of TiO_2 nanoparticles and simple doctor blading allows the production of a thin mesoporous layer of TiO_2 that becomes conductive upon high heat treatment. This porosity and nanostructure of it can be seen schematically in Fig. 1 but also is shown by SEM in Fig. 4. At high magnification, it is clear that the nanoparticles are on the scale of 15–25 nm in diameter. Prior work has shown that these particles have the anatase lattice geometry.

External quantum efficiency (EQE) curves of DSSCs composed from red raspberry juice applied to the TiO₂ is shown in Fig. 5B. EQE, also referred to as incident photon to converted electron (IPCE), is a metric to describe how many photons of a given wavelength successfully create electrons by the device. These electrons migrate to the anode and are ejected into the circuit. As the DSSCs are scanned, in 10 nm increments from 375 to 675 nm, the photocurrent generated is measured. This analysis displays the specific wavelengths at which the device is creating energy. When compared to the absorption spectra displayed in Fig. 5B and C, it can be seen that the maximum IPCE is blue shifted from the maximum absorbance of the raspberry dye alone, by approximately 20 nm. Similar analysis of the TiO₂ alone shows its characteristic activity at ~350 nm and no activity in the region of the anthocyanin's.

Results of investigation of anthocyanin-based DSSCs are presented in Fig. 6A and B. Fig. 4A demonstrates the relationship between temperature and photocurrent for this cell.



Fig. 5 – EQE of DSSCs and absorption curve of red raspberry juice. A) EQE spectra of DSSC without pigment, showing TiO_2 photon conversion in the UV region, note lack of activity from TiO_2 in conversion region of raspberry DSSC. B) EQE of DSSC sensitized with raspberry juice, averaged over 9 scans. Error bars indicate standard deviation across all measurements for given wavelength. C) Absorption spectra of raspberry juice measured by UV–vis spectrophotometer.

The upper graph characterizes a kinetic curve of photocurrent. It shows how photocurrent changes with time. The lower graph demonstrates how the temperature was altered over time during the experiment. One can see that at high temperature, current decreases over a given range of temperatures. DSSCs generate 1.69 μ A at 21.4 °C and 1.34 μ A at 39.5 °C. However, this decrease is reversible; current increases as temperature decreases across this temperature range.

Behavior of photocurrent generated by the DSSC under varied light intensities is illustrated in Fig. 4B. Dark current generated due to dark redox-reactions at the electrodes of DSSCs was equal to $0.34 \pm 0.1 \ \mu$ A. 30 s after the light (I_{light} = 20.6 quantum μ mol m⁻² s⁻¹) was switched on, current increased to 0.84 \pm 0.1 μ A. Further, with this illumination, current reached 0.88 μ A. Then, light intensity increased from 20.6 \pm 0.2 to 59.5 \pm 0.7 quantum μ mol m⁻² s⁻¹. Along with this, photocurrent jumped up to 1.54 μ A for 25 s. This value remained constant for 4 min. Upon increase of light intensity once again, to 95.6 \pm 1.1 quantum μ mol m⁻² s⁻¹, current increased to 1.75 μ A for 10 s. Similarly, this value remained constant for 4 min as well. When

the light was turned off, photocurrent decreased to $0.43\,\mu\text{A}$ and remained steady for 5 min.

Results of measuring temperature and light susceptibility of thylakoid-based SCs are illustrated in Fig. 6C and D, respectively. Photocurrent decreased from 0.46 μ A to 0.26 μ A, whereas the temperature increased from 24 °C to 39 °C. Photocurrent increased to 0.46 μ A for the subsequent temperature decrease to 23 °C.

Dark current for this cell was 0.07 μ A at the temperature 26 \pm 1 °C. Under minimal light intensity, photocurrent increased to 0.26 μ A, then decreased to 0.21 μ A for 4 min. It had not yet achieved stationary state. Increasing the light intensity, photocurrent jumped up to 0.34 μ A for less than 10 s then decreased to 0.29 μ A for 4 min. During the next increasing of light intensity, photocurrent climbed to 0.37 μ A, then decreased to 0.33 μ A for 4 min. After the light was turned off, the current fell to 0.01 μ A for 1 min.

Results of the investigation of spectral dependence of photocurrent for both types of cells are given in Table 1. For anthocyanin-based SCs, maximum photocurrent was



Fig. 6 – Photocurrent kinetics of DSSC. (A, B) raspberry extracts (anthocyanin-based DSSC) and (C, D) thylakoid preparations with: A, C – temperature altering; B, D – light intensity altering. Vertical short arrows on b and d indicate light turning on (1), light increasing (2,3), light turning off (downward arrows).

generated under blue light irradiation, with a slight decrease in photocurrent generated under green light, and the least photocurrent generated under red light. For thylakoid-based SCs, maximum photocurrent was generated under blue light, less photocurrent was generated under the red light, and the least photocurrent was generated under the green light. Measurement error is <7%.

Discussion

The results presented here indicate that the experimental setup design allows for the direct measurement of real operating conditions of the electrochemical cell which uses solar radiation energy. Preliminary results suggesting photocurrent dependence on temperature and the incident light intensity

Table 1 – Spectral dependence of photocurrent.							
Color light filter	The half-width of the passband, nm	DSSC type					
		Thylakoid-based DSSC	anthocyanin-based DSSC				
		Photocurrent, nA					
Blue-green	370–540	37,3 ± 2,6	105,7 ± 7,3				
Green—yellow	520-582	16,0 ± 1,2	$100,4 \pm 7,4$				
Orange-red and Red	606-710	27,5 ± 1,9	57,5 ± 4,0				

were obtained using this set-up. In the temperature range investigated here, the data are consistent with previously published results [10]. At temperatures ranging from 20 to 40 °C, current was reversible proportional to temperature. Since the decrease in current induced by the increase of temperature is reversible, one can conclude that the main mechanism of this reduction in photocurrent is not thermoinhibition, but reversible acceleration of the electron transfer from the conduction band of TiO₂ to the oxidized form of the iodine-based redox couple. The current amplitude generated in the thylakoid-based SC is 3-4 times smaller than that generated by the raspberry-based SC at the same temperature and light intensity. This may be due to the lower absorption cross-section of the thylakoid-based SCs compared to raspberry-based SCs. This low absorption crosssection may be due to the very large size of the thylakoid clusters compared to the average pore size of TiO₂, with a large portion of the TiO₂ pores presumably remaining unoccupied by thylakoid membrane sensitizer. In addition, the thylakoid-based cells are more inert: the delay of current changes in response to temperature changes can be up to a few minutes before achieving a plateau (Fig. 4C). At the same time, for the raspberry-based cells, after temperature equilibration, current plateaus within 10-20 s, and slowly begins to rise (Fig. 4A). In the thylakoid-based cells inertia may be associated with a significant contribution of the slow recombination reaction between TiO₂ and the electrolyte, which takes place at the expense of a large area of TiO₂ not covered by the dye (Fig. 1). At the same time, temperature-induced variations of current in the raspberry-based cells are related with a greater reduction of oxidized dye molecules by electrons from TiO₂, since the continuous dye coating makes electron transfer from TiO_2 to the electrolyte difficult (Fig. 1). Kinetic curves show current changing due to changes in light intensity, reaching a new peak after the increase in light intensity. The current generated by the raspberry-based cells remained nearly constant after the new maximum was reached, until the next light step. After the current yielded from the thylakoid-based cells reaches maximum level, it starts to decrease. This can also be attributed to the slow response of the electron leakage from TiO₂ to electrolyte. This situation can be described by the following sequence of events in DSSC: 1) Increase of the light intensity leads to increase in the frequency of the electron injection into the conduction band of TiO₂; 2) The concentration of electrons in the conduction band is increased, and therefore the likelihood of reduction of electrolyte is increased. But this reaction is slower than electron transfer to a coated glass electrode inside TiO₂ [10], so we can see its effect only after reaching the maximum photocurrent.

In the raspberry-based cells, back electron donation from TiO_2 presumably into electrolyte is extremely low. The main electron recombination occurs from TiO_2 onto the oxidized molecules of dye (Fig. 1). However, this reaction is much faster than the previous one. It is possible that in this case, the photocurrent increases to maximum level and reaches a plateau. As it follows from the results of photocurrent spectral analysis, both types of cells behave in accordance with the absorbance spectra of their sensitizers [16,22]. Further, the blue shift in the EQE compared to the absorption spectra of the

raspberry dye alone may be attributed to the electronic properties of the semiconductor layer of TiO_2 perturbing the electronic state of the anthocyanin molecule in the dye. Alternatively, only a subset of the total extracted anthocyanin pigments may either selectively attach or coat the TiO_2 particles or function as effective dyes for electron transfer into the TiO_2 .

Conclusion

We have designed a laboratory set-up that allows the measurement of photocurrent over varied operating conditions of the electrochemical cell. The set-up is highly sensitive, and is capable of recording minute changes in current with a resolution of 10 nA. Utilizing this experimental set-up, we have obtained the preliminary results of current dependence with regard to ambient temperature and the intensity of incident light, which correlates well with previously published results. This demonstrates reliability of results obtained by the laboratory set-up and its wide opportunities in analysis and characterization of these biologically incorporated SC devices moving forward.

Further development of the techniques described here involves the modernization of the laboratory set-up, to develop automated control and measuring processes. The authors suggest improving of the laboratory set-up by integrating the following elements into this system:

- A Peltier element (thermoelectric generator) with sufficient power output connected to a regulated power supply in order to achieve more accurate and steady maintenance of temperature.
- 2. The use of LED lamps with intensity control, for automated change of light parameters. These investigators intend to continue research into system automation by setting initial parameters via computer interface on the upgraded laboratory set-up. Research is intended to be carried out in a wider temperature range (-10 to 90 °C), under different light intensities and spectral properties using the updated LED lamps, replacing the need for light filters or multiple light sources.
- 3. Investigation of light and temperature effects on the DSSC containing different types of pigments is of interest. Wide variety of pigments would expand absorption spectra of solar cell. Temperature depending on efficiency of the solar cell may be different according to the pigment composition of dye. From this point of view, components of photosynthetic apparatus of Chl *f* and Chl *d*-containing cyanobacteria are attractive, as the long-wavelength maximum in the absorption spectrum of Chl *d* and Chl *f* is shifted towards longer wavelengths. In addition, it is possible to design measuring system for the investigation of DS-PECs based on the construction of our laboratory set-up.

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