PHOTOBIOELECTROCHEMICAL HYDROGEN AND ELECTRICITY PRODUCTION FROM DIFFERENT ORGANIC WASTES

L.S. ZUBCHENKO
National technical university of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute"
yellowjackets@ukr.net

Water treatment technology is one of the bioelectrochemical systems applications and is widely developed by many research laboratories all over the world. Using photoelectrochemical cells as an additional energy source allows the production of hydrogen in photobioelectrochemical systems without any external energy impacts.

Microorganisms-exoelectrogens, present on the anode of photobioelectrochemical systems, are universal biocatalysts. Almost any organic compound can be consumed by microorganisms and used for respiration resulting in electrical current generation.

This study analyses the performance of hydrogen generation in the photobioelectrochemical system. Cathodic hydrogen recovery and overall performance of hydrogen production were estimated for the system, operated with substrate concentrations: 5mM, 7.5 mM, 10 mM. A silicon solar cell was used as an additional energy source for the system. High efficiency of organic component destruction allows one to recommend photobioelectrochemical systems as an effective way for organic pollutants remediation with simultaneous hydrogen generation.

Bioelectrochemistry as a scientific field evolves on the intersection of biology and electrochemistry and illustrates the electrochemical processes, occurring in living systems. The intensive studies of resent decades have convincingly demonstrated that biological processes, especially associated with energy transformation, have electrochemical nature. Electrochemistry has found a new and extremely productive application in biology [1].

The beginning of bioelectrochemistry development could be dated back to the 1780s, when Galvani discovered electrical nature of the force, which caused reduction of the muscles (current from a static electricity generator could cause a severed frog's leg to twitch). Grove's experiments showed that the electrolysis process can be turned back to produce water molecule from H_2 and O_2 with simultaneous current generation. Almost two centuries later, in 1910, M.C. Potter observed electricity production, which happened to be the beginning of research into microbial fuel cells and bioelectrochemical systems [2].

In the bioelectrochemical systems (BES), like in the fuel cell, the reaction of substrate oxidation occurs at the anode and a proton reduction reaction occurs at the cathode. The oxidation of organic matter releases electrons, which move to the cathode via the external circuit doing electrical work. The circuit is completed by the movement of a compensating charge through the electrolyte often in the form of protons.

According to their function, bioelectrochemical systems are divided into microbial fuel cells (MFC), used for generating electricity, and microbial electrolysis cells (MEC), used for producing hydrogen.

The working principle of photobioelectrochemical systems lays in the connection of energy, harnessed from sunlight, with energy, generated during organic substrate oxidation. There is a large group of microorganisms (so called exoelectrogens) with a specific metabolism feature. During respiration process they can produce electrons and protons and transfer them out of the cell. In BES electrons, generated by microorganisms, are transferred to the anode and then, through the electric circuit, to the cathode.

In the microbial fuel cells protons, released from the substrate, recombine with oxygen forming the water molecule. In microbial electrolysis cells (bioelectrochemical systems for hydrogen generation) hydrogen is produced in reduction process on the cathode, therefore additional voltage should be supplied to the circle, to overcome the thermodynamical barrier of hydrogen generation [2].

Nowadays, many researches are focused on development of the photobioelectrochemical systems (PBES), which employ whole photoelectrochemical solar cells or photoelectrode, to provide the additional energy for bioelectrochemical hydrogen generation [3-6].

The possibility of application of dye-sensitized solar cell (DSSC) to power the microbial electrolysis cell (MEC) was demonstrated. Stable hydrogen generation was obtained without an external energy source. DSSCs, created by the combination of ruthenium dye-loaded TiO_2 film and platinized FTO glass, with an I^-/I_3^- redox couple, was used as an alternative bias (V_{oc} = 0.65 V). Hydrogen conversion efficiency for this cell reached 71.3−77.0% (for the plain cathode) and 79.3−82.0% (Pt-loaded carbon felt) at >0.7 V [3].

It is also possible to connect DSSC to multiple MECs (multiple MECs were feeding from single DSSC). Hydrogen production occurred simultaneously in all the connected MECs with substrate (acetate) to hydrogen conversion efficiencies ranging from 42% to 65%. The system produced hydrogen when the solar cell was irradiated with light [4].

As described in [5], in PBES with DSSC electrochemically active microorganisms generate electrons in the oxidation process of organic compounds. Electrons are transferred to the anode by extracellular structures of microorganisms and then proceed to the external circuit.

Electrons produced by microorganisms regenerate the oxidized dye molecules of the DSSC.

On irritation, the electrons in ruthenium-dye molecules of DSSC are excited. Electrons, withdrawn from the dye molecule, are injected into the conduction band of the titanium dioxide nanoparticles, sintered on the photoelectrode of the solar cell.

The injected electrons are rapidly transferred from the TiO_2 photocathode to the cathode of the MEC. This raises the Fermi energy of the MEC cathode, reaching high enough level to reduce protons at pH 7.0. Excited electrons from the photo-electrode of the solar cells are involved in hydrogen production on the MEC cathode.

It is also shown that DSSC (Voc 602 mV) can produce hydrogen only when the electrochemically active bacteria oxidize nutrient substrate with simultaneous electrical current generation. When the experiment was performed without acetate, the cathode potential of the MEC was around −340 mV vs Ag/AgCl on light irradiation. This potential is too high to reduce protons at neutral pH (7.0) [5].

In another study [7] the photobioelectrochemical system, based on p-type Cu_2O nanowire-arrayed photocathode, was investigated. The MEC based on the synergistic effect of the bioanode and photocathode demonstrated a substantial current generation of 200 μA at zero bias under a white light illumination of 20 mW/cm^2. In this device, the photocathode and bioanode were interfaced by matching the redox potentials of bacterial cells and the electronic bands of semiconductor nanowires [7].

Microorganisms-exoelectrogens can consume a wide range of organic compounds including sugars (glucose, sucrose, xylose), organic acids (acetic, formic, propionic), carbohydrates, fatty acids etc.

Not only simple substances can be consumed by microbial association, growing on the anode, but also complex substrates such as wastewater, liquid organic waste, landfill leaches. When not only exoelectrogens are present in the anode biofilm association, the efficiency of substrate consumption will be better (the variety of metabolic ways allows conversion of more types of compounds), but hydrogen production can be low. Most organisms which were found in the anode biofilm were able to convert organic compounds into acetates. Only a small group of microorganisms (including exoelectrogens) can consume acetates. So, an acetate is often used as a nutrient source for experimental purposes.

Research methodology

Hydrogen production process was carried out in a two-chamber photobioelectrochemical system with the proton-exchange membrane Nafion. The anode was an electrode of carbon felt, the cathode was a

carbon felt coated with platinum. The silicon solar cell was connected to the bioelectrochemical system, to supply additional voltage for hydrogen generation. The following composition was used as anodic solution, g/dm^3: NaH_2PO_4 – 2.13; Na_2HPO_4 – 4.58;NH_4Cl – 0.31; KCl – 0.13. Basic solution also contained trace mineral and vitamin solutions to provide for vital functions of microorganisms [8]. The enrichment of the anode biofilm was performed as described in [8]. The system operated in a bath-mode. The duration of the cycle was determined by the residual amount of nutrient substrate. New cycles were started after reducing the COD (chemical oxygen demand) level below 50 mg COD/dm^3.

The voltage, generated by PBES, was measured by a digital multimeter. PBES was coupled with the gas storage tube, and the system for volumetric gas production monitoring. The voltage, generated by FBES, current, change of internal resistance and the volume of produced hydrogen were measured once a day.

The estimation of losses, which occur in the system is an important step in the bioelectrochemical systems evaluation. It also allows predicting the efficiency of the system operation, detecting some problems and bottlenecks in its design, operation conditions etc. The maximum cell voltage (theoretical electromotive force or open circuit voltage) that can be generated in the cell operating reversibly is defined as the equilibrium cell potential E_t, = (Ec-Ea), which is the difference between the ideal equilibrium potentials of the cathode and anode (estimated by Nernst equation). Consequently, in real bioelectrochemical systems the cell voltage is always lower because of the losses caused by the irreversibilities. Thus, polarization losses appear from these three sources: ohmic losses, activation losses and concentration losses. Polarization losses have the main influence on the voltage.

The actual voltage of bioelectrochemical system can be calculated as the difference between the theoretical electromotive force and polarization losses.

The electrochemical balance of the bioelectrochemical system can be written as:

$$V=E_t – \eta_{omh} – \eta_{conc} – \eta_{act} \quad (1)$$

where V is the cell voltage V; E_t is the theoretical electromotive force (E_{EMF}) for the MFC and the counter electromotive force (E_{CEF}) for the MEC; V; η_{omh} is the ohmic losses, V; η_{conc} is the concentration losses; V; η_{act} is the activation losses, V.

Since, for the bioelectrochemical system for hydrogen production (MEC) V=– E_{ap} (E_{ap} – the value of applied voltage), the electrochemical balance of the cell can be estimated:

$$– E_{ap} =E_{CEF} – \eta_{omh} – \eta_{conc} – \eta_{act} \quad (2)$$

For the photobioelectrochemical system E_{ap} will be equal to the generated photovoltage.

For estimation of hydrogen production efficiency the following parameters were used:

Volumetric hydrogen production rate, $m^3H_2/(m^3 \cdot day)$:

$$Q = \frac{V_{H_2}}{VT}, \quad (3)$$

were V_{H2} is the volume of produced H_2, m^3; V is the volume of the reactor, m^3; T is the time, day.

Columbic efficiency, % :

$$CE = \frac{\nu_{CE}}{\nu_t}, \quad (4)$$

where ν_{CE} is the moles of hydrogen recombined in BES, estimated by current:

$$\nu_{CE} = \frac{\int_{t=0}^{t} Idt}{2F}, \quad (5)$$

where $I = V/R_{ex}$ is the current, calculated from the voltage applied to the resistor (R= 6 Ω), A; F = 96 485, Faraday constant, A·sec·/mole⁻(or C/ mole⁻); t is the interval of data collection, sec.

ν_t is the total theoretical moles of hydrogen that can be obtained, mol.

The theoretical volumetric hydrogen production rate, $m^3 \cdot H_2/(m^3 \cdot day)$, was calculated using the chemical oxygen demand:

$$\nu_t = \frac{b_{H_2} V \Delta COD}{M}, \quad (6)$$

where b = 4 is the maximum stoichiometric yield of hydrogen, per 1 mole of substrate, mol/mol; ΔCOD is the chemical oxygen demand difference value between the beginning and end of cultivation, g COD/dm^3; M is the molecular weight of sodium acetate, 82.g/mol.

The cathodic hydrogen recombination, %, can be determined as:

$$r_{cat} = \frac{\nu_{H_2}}{\nu_{CE}}, \quad (7)$$

where v_{H_2} is the moles of produced H_2;

The performance of hydrogen generation, %, was calculated according to the equation:

$$P_{H_2} = r_{cat} CE, \quad (8)$$

For MEC, the hydrogen production rate (cm^3H_2/day) can be described by the equation:

$$Q_{H_2} = Y_{H_2}\left(\frac{I_{BES}}{mF}\frac{RT}{P}\right), \quad (9)$$

where Y_{H2} –is dimensionless cathode efficiency; I_{MEC} is the MEC current, A; F is the Faraday constant, C/mol (or A·sec·/mole^{-}); R is the ideal gas constant, J/(mol·K); P is the MEC pressure, atm; T is the operation temperature, K.

Results and Discussion

The operational parameters of the photobioelectrochemical system were estimated for different concentrations of sodium acetate, mM: 5; 7,5; 10. After adding the sodium acetate to the anodic chamber of bioelectrochemical cell a slight current generation was observed. A few hours later, after stabilization of the current generation, the photoelectrochemical cell was connected to the MEC. The working voltage of photoelectrochemical cell was 0,4 V.

Hydrogen production was obtained from the first day of the system operation. The diagram presented in the Figure shows main efficiency indexes for different substrate concentrations.

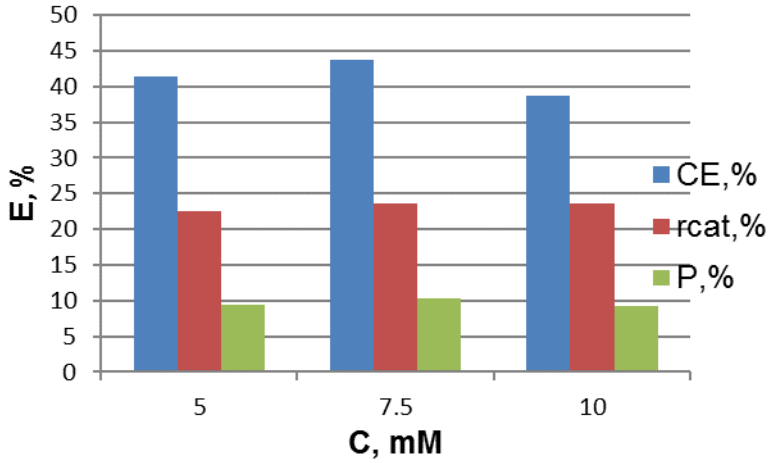

Fig. Hydrogen production efficiency for photobioelectrochemical systems operation with different substrate concentrations

The analysis of experimental data shows that Columbic efficiency varied at the level of 40 – 45 %, and the highest level was for 7,5 mM concentration of sodium acetate. The cathodic hydrogen recombination had very close values for all concentrations, indicating the system's stability. The decrease in the Columbic efficiency at 10mM can be caused by a high growth rate of microorganisms. The increasing growth rate of microorganisms requires more energy for the building of cellular structures. Thus, COD decreases rapidly without hydrogen generation. To confirm this statement, additional experiments or modeling should be conducted.

Despite the small value of Columbic efficiency at 10mM, the overall performance of PBES was better for higher concentrations of sodium acetate.

Hydrogen yield estimated by the COD removal efficiency in PBES was unstable. The maximum values of hydrogen yield were obtained on the first two days of experiment. The maximum hydrogen yield reached 0,015 gH_2/gCOD at a concentration of 10 mM.

Conclusions

In this study, hydrogen production performance in the photobioelectrochemical system was determined. The Columbic efficiency, cathodic hydrogen recombination and overall performance for different concentrations of sodium acetate as a single component of nutrient medium were estimated. Maximal overall performance of 44% was obtained for sodium acetate at a concentration of for 7.5 mM. High efficiency of the COD decrease confirms the possibility of using photobioelectrochemical systems for high concentrated wastewater treatment.

References

[1] Kuzminskiy Ye., Shchurska K., Samarukha I., Lagod G., Bioelectrochemical hydrogen and electricity production. Theoretical bases, description and modeling of the process, Politechnica Lubelska, 2013.

[2] Bullen R.A., Arnot T.C., Lakemanc J.B., Walsh F.C., Biofuel cells and their development, Biosensors and Bioelectronics, 21, 2015–2045, 2006.

[3] Chae K.J., Choi M.J., Kim K.Y., Ajayi F. F., Chang In S. , Kim In S., A solar-powered microbial electrolysis cell with a platinum catalyst-free cathode to produce hydrogen, Environ. Sci. Technol., 43 (24), 9525–9530, 2009.

[4] Ajayi F.F., Kim K.Y., Chae K.J., Choi M.J., Chang In S., Kim In S. Optimization studies of biohydrogen production in a coupled microbial electrolysis-dye sensitized solar cell system, Official journal of the European Photochemistry Association and the European Society for Photobiology, 9, 3, 349 –356, 2010.

[5] Ajayi F. F., Kim K.Y., Chae K.J., Choi M. J., Kim S.Y., Chang In S., Kim In S., Study of hydrogen production in light assisted microbial electrolysis cell operated with dye sensitized solar cell. International Journal of Hydrogen Energy, 34, 23, 9297–9304, 2009.

[6] Anhuai L., Yan L., Song J., Hongrui D., Cuiping Z., Xin W. Changqiu W., Microbial Fuel Cell Equipped with a Photocatalytic Rutile-Coated Cathode, Energy Fuels, 24, 2, 1184 –1190, 2010.

[7] Qian. F., Gongming W., Yat L., Solar-Driven Microbial Photoelectrochemical Cells with a Nanowire Photocathode,Nano Lett. 10, 4686 – 4691, 2010.

[8] Zubchenko L.,Kuzminskiy Ye. Characteristics of biofilm formation process in the bioelectrochemical systems, working in batch-mode of cultivation, Chem. Chem. Technol., 11, 1, 105 –110, 2017.