

One more function for microbial fuel cells in treating wastewater: producing high-quality water

ZHEN HE – Department of Civil Engineering and Mechanics, University of Wisconsin-Milwaukee, USA

Please cite as: CHEMIK 2012, 66, 1, 3-10

Introduction

The mission of wastewater treatment has transformed from simple contaminant removal to a more sustainable task with the goals to consume less energy and recover more water. Reducing energy consumption requires a more efficient treatment process and/or recovery of energy from contaminants, and recovering more water requires extensive post-treatment, usually through membrane processes, to extract high-quality water for reuse. However, at this time, no single treatment technology can simultaneously accomplish wastewater treatment, bioenergy production, and water recovery.

Microbial fuel cells (MFCs) have gained significant attention because of their integrated wastewater treatment and bioenergy production. MFCs are bio-electrochemical reactors in which bacteria oxidize various organic or inorganic compounds in the anode compartment and generate protons and electrons that transport to the cathode to reduce oxygen to water [1]. Electron flow from the anode to the cathode generates an electric current or power if a load is connected (Fig. 1). Direct electricity generation from organic contaminants makes MFCs a promising approach for wastewater treatment, although some key issues, such as optimal reaction configuration, the cost of catalysts and electrodes, and better understanding of microbial activities, need to be addressed before practical application.

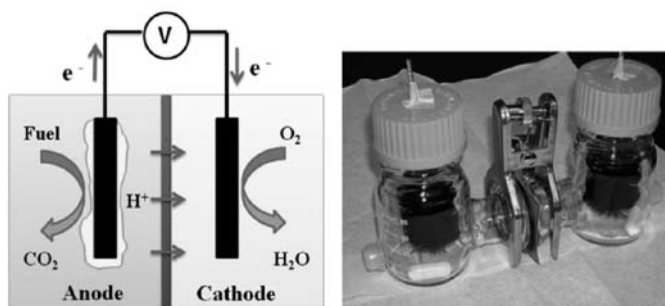


Fig. 1. Schematic and lab-prototype of microbial fuel cells

In general, MFC research focuses on reactor architecture, microbiology, and electrochemistry:

(a) Conventional MFC configuration is two-chamber H type, which derived from chemical fuel cells. These MFCs are simple and can be easily built for basic studies, but they are not suitable for wastewater treatment. Consequently, many configurations specially designed for wastewater treatment were reported. For instance, upflow MFCs that adopted the flow pattern from upflow anaerobic sludge blanket (UASB) have been proven as an efficient configuration for electricity generation and organic removal [2,3]. The air-cathode MFCs omit ion exchange membranes and can reduce internal resistance, thereby increasing electricity generation [4], but their scalability remains challengeable.

- (b) Microorganisms act as biocatalysts in MFCs; therefore, understanding their behavior is critical to improving MFC performance. Microbiological studies have attempted to answer why microbes can transfer electrons from/to an electrode and how electrons are transferred. Three mechanisms are proposed based on pure culture studies: 1) direct electron transfer through membrane-binding proteins; 2) mediated electron transfer with the aid of soluble electron shuttles; and 3) electron transfer via bacterial nanowires [5, 6]. Electrochemically active organisms such as *Geobacter spp.* and *Shewanella spp.* are widely used as model organisms to study electron transfer [7, 8]. Microbiological studies of mixed culture are used to map microbial community on the electrode, identify the dominant species, and isolate new strains that are electrochemically active [9].
- (c) Electrochemistry plays an important role in understanding the limiting factors on MFC performance. Electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are applied to identify electrochemical activities on the electrode [10] and obtain sensitive results on internal resistance of an MFC [11].

This paper will briefly discuss the potential approaches to produce high-quality water in MFCs when treating wastewater. The discussion will focus exclusively on MFCs, although new bioelectrochemical systems, such as microbial electrolysis cells (MECs) [12] and microbial desalination cells (MDCs) [13], have been developed from MFCs.

Conventional functions of MFCs

MFCs are designed mainly for two purposes: removing contaminants and producing energy. Contaminant removal is the primary function of MFCs, because they are essentially a process for wastewater treatment. Variety substrates have been investigated in the anode of MFCs, including simple organics such as acetate and glucose, and complex compounds like actual wastewater and petroleum compounds. MFCs can also remove inorganic compounds such as nitrate via bioelectrochemical denitrification. More information about the substrates for MFCs can be found in a previous review article [14]. During contaminant removal, bioelectricity is produced as a result of bioelectrochemical reactions. To compete with anaerobic digester, which is commonly employed to harvest bioenergy (biogas) from wastewater, MFCs need to achieve power production above 250 W/m³. This threshold value has been reached in small-scale MFCs (a few to several hundred milliliters), but larger reactors with a volume over several liters usually produce a much smaller power density, except when a precise condition such as pure oxygen is applied. Satisfactory energy production in large-scale MFCs will determine the commercial feasibility of this technology.

New function of producing high-quality water

An important issue that has been ignored by previous MFC studies is the fate of the treated effluent. Clearly, turning this effluent into high-quality water will meet the increasing demand for water reuse

and help create a more sustainable wastewater treatment system. There are two approaches to produce high-quality water from MFCs: first, the MFC (anode) effluent can be further polished by additional membrane processes such as micro-, ultra-, and nano-filtrations and reverse osmosis (RO). Second, some of those membrane processes can be integrated into MFCs with additional benefits. We believe the second approach will be of strong interest to MFC development; therefore, the following sections focus on the integrated system for water production.

We have investigated the integrated MFC systems from two aspects, depending on the membrane type. The first aspect is to develop MFCs similarly to anaerobic membrane bioreactors (AMBRs) using micro/ultra filtration membranes to separate anode and cathode compartments (Fig. 2). Because of the requirement of oxygen supply to cathodes, this type of MFC cannot be operated with vacuum extraction of water in the cathode like that in most MBRs/AMBRs. Instead, a hydraulic pressure will be employed to push the anode solution through the filtration membrane. The use of positive pressure is advantageous because it eliminates the need for aeration in the cathode compartment, because passive air supply is realized and water seepage can wet the cathode electrode. Our preliminary study has demonstrated the feasibility of this concept and further data collection is in the process. Our second aspect is to integrate forward osmosis into MFCs, forming osmotic MFCs (OsMFCs). OsMFCs are attractive because of the rapid development and use in forward osmosis. To better understand OsMFCs, one needs to understand forward osmosis, which is briefly introduced below.

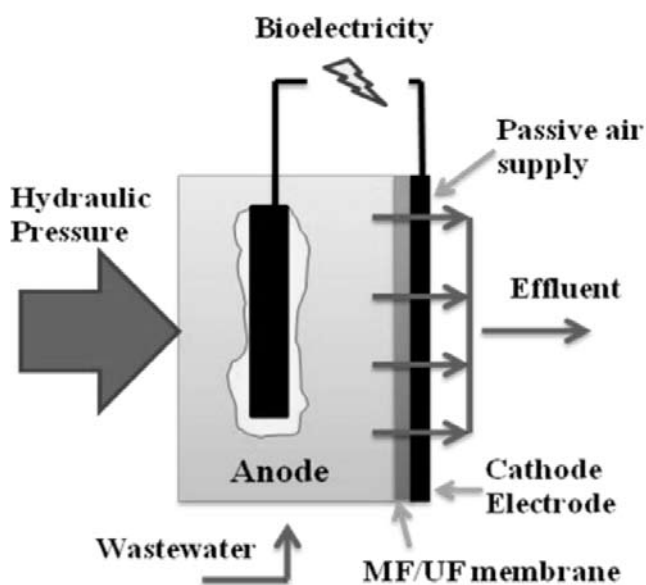


Fig. 2. MFCs using a micro- or ultra-filtration membrane as separator for water extraction under a hydraulic pressure

Forward osmosis

Forward osmosis (FO) is the movement of water through a semi-permeable membrane driven by water-osmotic pressure [15,16]. The concentrated solution (draw solution) on the permeate side of the membrane, which should have a high osmotic efficiency, creates osmotic pressure. Draw solutions should be separated easily and inexpensively from the solution, leaving potable water [17]. Figure 3 shows the flow of solvent in forward osmosis and reverse osmosis (RO). Compared with pressure-driven membrane processes such as RO, FO can be operated at a low hydraulic pressure, exhibit a high rejection rate of a wide range of contaminants, and has less membrane fouling [15].

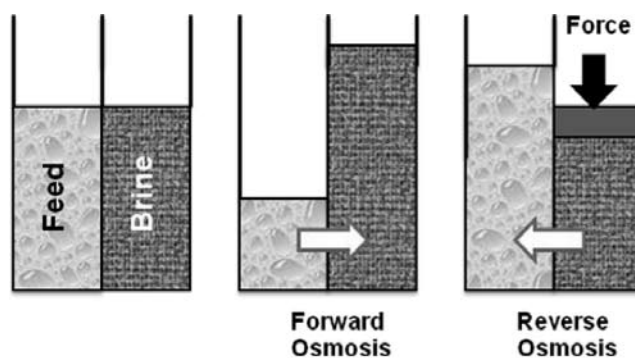


Fig. 3. Solvent flow in forward osmosis and reverse osmosis

The study of FO technology has focused on membrane development, draw solutions, and applications. The FO membranes consist of dense, non-porous, and selectively permeable materials [15, 18,19]. Various chemicals have been suggested and tested as draw solutions, including sulfur dioxide, aluminum sulfate, glucose, potassium nitrate, a mixture of ammonia and carbon dioxide, and recently developed magnetic nanoparticles [15, 20÷23]. FO technology has been investigated for producing high-quality water from wastewater, landfill leachate, and digester centrate [24÷27], and it has also been used for seawater desalination, the pharmaceutical industry, food processing, and the production of osmotic electric power [28÷31].

Osmotic microbial fuel cells (OsMFCs)

The key criteria of a sustainable wastewater treatment technology include the following:

- (a) efficient contaminant removal as the primary goal of most wastewater treatment processes.
- (b) energy recovery to generate useful energy from organic wastes and offset energy consumption by the treatment system; and c) water recovery to produce high-quality water for water reuse or other purposes that can reduce water demand and consequently wastewater production. Both MFC and FO technologies have their own drawbacks and cannot meet all the criteria individually.

- MFCs can deal with various contaminants in wastewater and generate bio-electricity that is potentially useful, but they are unable to produce high-quality water for water reuse without extensive post-treatment
- FO technology can extract high-quality water from wastewater, but the remaining (organic) concentrates from FO processes still require treatment, which usually employs aerobic biodegradation [32]. Energy contents in organic contaminants are not recovered during aerobic treatment.

A synergetic combination of these two “apparently irrelevant” technologies may potentially complement each other and lead to a sustainable wastewater treatment technology. It is technically feasible to integrate FO into an MFC to form an osmotic microbial fuel cell (OsMFC) for simultaneous water extraction, wastewater treatment, and bioenergy production (Fig. 4). The anode of an OsMFC is same as a conventional MFC, treating wastewater via bioelectrochemical reactions, while its cathode contains a high-salinity catholyte as the draw solution [33]. An FO membrane acts as a separator between the anode and the cathode, and the advantages and benefits of such a combination and development include:

- High-quality water can be extracted from the wastewater through the FO process
- Water flux through the FO membrane could promote proton transport that can buffer the catholyte and thus potentially increase electricity generation
- The concentrated organic wastes can be oxidized with the production of bioelectricity

- Both FO membrane and the water flux can prevent oxygen diffusion into the anode, thereby creating an anaerobic condition for anode reactions.

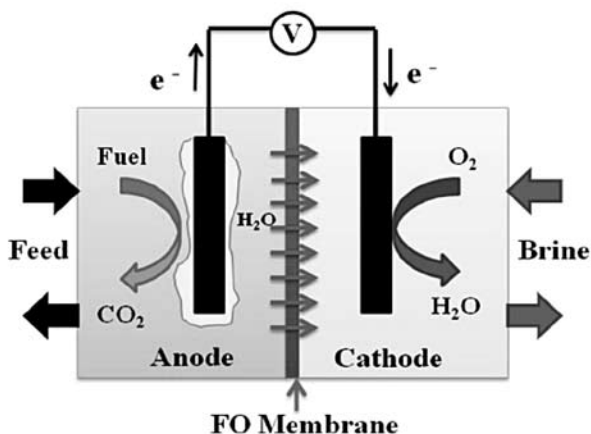


Fig. 4. Schematic of an osmotic microbial fuel cell

The potential applications of OsMFCs are water reuse and seawater desalination.

- OsMFCs inherit the function of water reuse from FO development with additional bioenergy recovery. A special requirement for water reuse is re-concentrating and recycling the draw solution; therefore, additional treatment using RO is needed. There is the possibility to use electricity produced in OsMFCs to offset some energy consumption by the RO system, resulting in an energy-efficient system.
- The water production in OsMFCs can also be used to dilute seawater, reducing its salinity as well as energy requirement by the post-desalination processes. In this way, seawater will function as a draw solution without the need to recycle the draw solution. If OsMFCs are linked to MDCs [34], we can achieve an extensive wastewater treatment and maximized bioenergy production.

Our study has provided a proof-of-concept of an OsMFC for simultaneous wastewater treatment, water extraction, and bioenergy production [33]. The data showed that electricity production was observed in both an OsMFC and a conventional MFC (using cation exchange membrane as a separator) with either NaCl or seawater as a draw solution (catholyte), demonstrating that FO membranes can act as a separator in MFCs without decreasing electricity generation. In general, the OsMFC produced more electricity than the MFC, especially with the high-salinity catholyte. It was found that water flux could transport protons from the anode to the cathode, supporting the cathode reaction and buffering the increased pH. We also found that some draw solutes that showed exceptional performance in FO process such as calcium chloride and sugar solution did not yield good electricity production in OsMFCs, because of the problems associated with membrane fouling or low conductivity.

The key to developing an efficient OsMFC system is to complement FO (e.g., water flux) and MFC (e.g., electricity generation) into a robust process, and a few important problems must be investigated and understood before we step into the practical stage of scaling up OsMFCs. For instance, the draw solution has dual roles in OsMFCs, creating osmotic pressure and providing medium for cathode reaction. An optimal draw solution (catholyte) for OsMFCs should meet a few criteria, including low cost, high conductivity for both water flux and electricity generation, environmental friendliness, and recovery with low energy consumption. Recent studies have identified water-soluble magnetic nanoparticles as a draw solute that can be recovered by magnetic field, instead of energy-intensive RO processes [22, 35]. This discovery can potentially revolutionize FO technology into a low-energy process and will be of great interest in the future application of OsMFCs. Another critical factor is membrane fouling, as the FO membrane is prone

to fouling compared with ion exchange membranes used in conventional MFCs. The FO membrane fouling can adversely affect water flux but increase electricity generation through increasing anode conductivity via reverse water (and salt) flux. The anti-fouling methods employed by FO processes must be examined for their feasibility in OsMFCs because of the presence of microorganisms in the anode.

Summary

The new function of producing high-quality water will make MFCs an attractive technology for sustainable wastewater treatment, but the research in this area is still in its infancy. Integrating water production into MFCs will generate additional benefits such as eliminating aeration, increasing conductivity of catholyte, and promoting transport of protons. The MFCs based on MF/UF or FO membranes should take advantage of the existing knowledge of AMBR and FO processes, and absorb those beneficial aspects. Nevertheless, significant effort will be required to develop those MFCs, and the new function warrants further research.

Literature

- Logan B.E., Hamelers B., Rozendal R.A.; Schroder U., Keller J., Freguia S., Aelterman P., Verstraete W., Rabaey K.: *Microbial fuel cells: methodology and technology*. Environmental Science and Technology 2006, **40**, 17, 5181-5192.
- He Z., Wagner N., Minteer S.D., Angenent L.T.: *An upflow microbial fuel cell with an interior cathode: assessment of the internal resistance by impedance spectroscopy*. Environmental Science & Technology 2006, **40**, 17, 5212-5217.
- Rabaey K., Clauwaert P., Aelterman P., Verstraete W.: *Tubular microbial fuel cells for efficient electricity generation*. Environmental Science and Technology 2005, **39**, 20, 8077-8082.
- Liu H., Logan B.E.: *Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane*. Environmental Science and Technology 2004, **38**, 14, 4040-6.
- Katz E.; Shipway A.N., Willner I.: *Biochemical fuel cells*. In Handbook of Fuel Cells - Fundamentals, Technology and Applications; Vielstich W., Gasteiger H.A., Lamm A., Eds. John Wiley & Sons, Ltd: 2003; Vol. 1.
- Gorby Y.A., Yanina S., McLean J.S., Rosso K.M., Moyles D., Dohnalkova A., Beveridge T.J., Chang I.S., Kim B.H., Kim K.S., Culley D.E., Reed S.B., Romine M.F., Saffarini D.A., Hill E.A., Shi L., Elias D.A., Kennedy D.W., Pinchuk G., Watanabe K., Ishii S., Logan B., Nealon K.H., Fredrickson J.K.: *Electrically conductive bacterial nanowires produced by Shewanella oneidensis strain MR-1 and other microorganisms*. Proceedings of the National Academy of Sciences of the United States of America 2006, **103**, 30, 11358-63.
- Lovley D.R.: *Microbial fuel cell: novel microbial physiologies and engineering approaches*. Current Opinion in Biotechnology 2006, **17**, 3, 327-332.
- Bretschger O., Obraztsova A., Sturm C.A., Chang, I.S., Gorby Y.A., Reed S.B., Culley D.E., Reardon C.L., Barua S., Romine M.F., Zhou J., Beliaev A.S., Bouhenni R., Saffarini D., Mansfeld F., Kim B.H., Fredrickson J.K., Nealon K.H.: *Current production and metal oxide reduction by Shewanella oneidensis MR-1 wild type and mutants*. Applied and Environmental Microbiology 2007, **73**, 21, 7003-7012.
- Logan B.E.: *Exoelectrogenic bacteria that power microbial fuel cells*. Nature Reviews Microbiology 2009, **7**, 5, 375-81.
- Fricke K., Harnisch F., Schroder U.: *On the use of cyclic voltammetry for the study of anodic electron transfer in microbial fuel cells*. Energy & Environmental Science 2008, **1**, 1, 144-147.
- He Z., Mansfeld F.: *Exploring the use of electrochemical impedance spectroscopy in microbial fuel cell studies*. Energy & Environmental Science 2009, **2**, 215-219.
- Logan B.E., Call D., Cheng S., Hamelers H.V., Sleutels T.H., Jeremiasse A.W., Rozendal R.A.: *Microbial electrolysis cells for high yield hydrogen gas production from organic matter*. Environmental Science & Technology 2008, **42**, 23, 8630-40.
- Cao X., Huang X., Liang P., Xiao K., Zhou Y., Zhang X., Logan B.E.: *A new method for water desalination using microbial desalination cells*. Environmental Science & Technology 2009, **43**, 18, 7148-52.
- Pant D., Van Bogaert G., Diels L., Vanbroekhoven K.: *A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production*. Bioresource Technology 2010, **101**, 6, 1533-1543.

15. Cath T.Y., Childress A.E., Elimelech M.: *Forward osmosis: principles, applications, and recent developments*. Journal of Membrane Science 2006, **281**, 70-87.
16. Ng H.Y., Tang W., Wong W.S.: *Performance of forward (direct) osmosis process: membrane structure and transport phenomenon*. Environmental Science & Technology 2006, **40**, 7, 2408-13.
17. McCutcheon J.R., Elimelech M.: *Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis*. Journal of Membrane Science 2006, **284**, 1-2, 237-247.
18. Yang Q., Wang K.Y., Chung T.S.: *Dual-layer hollow fibers with enhanced flux as novel forward osmosis membranes for water production*. Environmental Science & Technology 2009, **43**, 8, 2800-5.
19. Yip N.Y., Tiraferri A., Phillip W.A., Schiffman J.D., Elimelech M.: *High performance thin-film composite forward osmosis membrane*. Environmental Science & Technology 2010, **44**, 10, 3812-8.
20. Kravath R.E., Davis J.A.: *Desalination of seawater by direct osmosis*. Desalination 1975, **16**, 151-155.
21. McCutcheon J.R., McGinnis R.L., Elimelech M.: *A novel ammonia-carbon dioxide forward (direct) osmosis desalination process*. Desalination 2005, **174**, (1), 1-11.
22. Ling M.M., Wang K.Y., Chung T.S.: *Highly water-soluble magnetic nanoparticles as novel draw solutes in forward osmosis for water reuse*. Industrial & Engineering Chemistry Research 2010, **49**, 12, 5869-5876.
23. Li D., Zhang X., Yao J., Simon G.P., Wang H.: *Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination*. Chem Commun (Camb) 2011, **47**, 6, 1710-2.
24. Cath T.Y., Gormly S., Beaudry E.G., Flynn M.T., Adams V.D., Childress A.E.: *Membrane contactor processes for wastewater reclamation in space. I. direct osmotic concentration as pretreatment for reverse osmosis*. Journal of Membrane Science 2005, **257**, 85-98.
25. Cath T.Y., Childress A.E.: *Membrane contactor processes for wastewater reclamation in space. II. combined direct osmosis, osmotic distillation, and membrane distillation for treatment of metabolic wastewater*. Journal of Membrane Science 2005, **257**, 111-119.
26. Holloway R.W., Childress A.E., Dennett K.E., Cath T.Y.: *Forward osmosis for concentration of anaerobic digester centrate*. Water Research 2007, **41**, 17, 4005-14.
27. Cornelissen E.R., Harmsen D., Beerendonk E.F., Qin J.J., Oo H., de Korte K.F., Kappelhof J.W. M.N.: *The innovative osmotic membrane bioreactor (OMBR) for reuse of wastewater*. Water Science & Technology 2011, **63**, 8, 1557-1565.
28. Talaat K.M.: *Forward osmosis process for dialysis fluid regeneration*. Artificial Organs 2009, **33**, 12, 1133-5.
29. Leob S.: *Large-scale power production by pressure-retarded osmosis using river water and sea water passing through spiral modules*. Desalination 2002, **143**, 115-122.
30. Beaudry E.G., Lampi K.A.: *Membrane technology for direct osmosis concentration of fruit juice*. Food Technology 1990, **44**, 121.
31. Singer E.: *New technologies deliver in treating neurological diseases*. Natural Medicines 2004, **10**, 12, 1267.
32. Achilli A., Cath T.Y., Marchand E.A., Childress A.E.: *The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes*. Desalination 2009, **239**, 10-21.
33. Zhang F., Brastad K., He Z.: *Integrating forward osmosis into microbial fuel cells for wastewater treatment, water extraction and bioelectricity generation*. Environmental Science & Technology 2011, **45**, 6690-6696.
34. Jacobson K.S., Drew D., He Z.: *Use of a liter-scale microbial desalination cell as a platform to study bioelectrochemical desalination with salt solution or artificial seawater*. Environmental Science & Technology 2011, **45**, 4652-4657.
35. Liu Z., Bai H., Lee J., Sun D.D.: *A low-energy forward osmosis process to produce drinking water*. Energy & Environmental Science 2011, **4**, 2582-2585.

ZHEN HE – Ph.D., Assistant Professor of Civil Engineering at the University of Wisconsin-Milwaukee, USA. He received his B.S. from Tongji University, China, M.Sc from Technical University of Denmark, and Ph.D. from Washington University in St. Louis, USA, all in environmental engineering. His research focuses on sustainable water and wastewater treatment using bioelectrochemical technologies and bioenergy production from wastewater.

E-mail: zhenhe@uwm.edu

Kraków to host international meeting of young researchers

Doctoral students and young researchers from 33 countries will meet in March 2012 in Kraków. The main theme of the conference Eurodoc 2012 will be funding of education and research of young scientists. The conference organizers met with the Deputy Minister for Science Maria Orłowska. The European Council of Doctoral Candidates and Junior Researchers - Eurodoc is a federation of doctoral students and young researchers from 33 countries, members of the European Union or the European Council. It is based in Brussels. Eurodoc conferences are held every year in a different country. For the first time, the meeting will be held in Poland. Conference organizers will be AGH University of Technology, the Jagiellonian University and the National Representation of PhD Candidates in Poland.

Representation of PhD Candidates in Poland Kinga Kurowska during the meeting in Warsaw. She explained that one of the objectives of the Eurodoc 2012 conference is to organize the information on various funding opportunities. He added that the organizers of the Kraków conference would like to publish the conclusions of this meeting so that they can contribute to creating a more coherent and simpler system of support for young scientists - both in terms of research funding, as well as scholarships, exchange programs and post-doctoral internships. This would involve more countries than just EU member states, e.g. those cooperating in the Eastern Partnership. Deputy Minister for Science reminded that Poland during its Presidency proposed that PhD students should benefit more from the Erasmus exchange program. She added that differences between the systems and training programs in various countries sometimes hinder international exchange. The European Union did agree to begin the so-called Bologna process, which aims to standardise the organization of studies at three levels: undergraduate, master and doctoral. However, education methods and programs still differ. She reserved that a common base of skills and competencies of graduates of various universities is beneficial, but it should not deprive young researchers of an opportunity to develop their own ideas. The representative of the board of the European Council of Doctoral Candidates and Junior Researchers - Eurodoc, Elena Golovushkina noted that the mobility of young doctors is not limited to fellowships at foreign universities, but also includes, for example, jobs in private companies interested in developing innovative products.

(<http://www.naukawpolsce.pap.pl>, 15.11.2011)