# Reliable renewable energy – application of electrochemical capacitors for electrical energy storage

Anna DETTLAFF*, Monika WILAMOWSKA-ZAWŁOCKA, Ewa KLUGMANN-RADZIEMSKA - Faculty of Chemistry, Gdansk University of Technology, Gdansk, Poland

Please cite as: CHEMIK 2016, **70**, 5, 247–254



## Introduction

According to the United Nations projections of population growth, the world population of humans will reach 13 billion at the end of the XXI[st] century. The population growth consequently leads to increased demand for electrical energy, which results in greater interest in renewable energy sources. Unfortunately, in this case, conversion of the energy strongly depends on weather conditions and less on the human activity. This applies in particular to the solar and wind power plants. The accumulation of energy by conversion of electrical energy to chemical energy is one way to reverse this unfavourable situation. Such conversion allows to store the energy surplus and to utilize it in the energy deficit period. Production and development of existing energy storage devices is necessary to move away from conventional energy sources to renewable ones.

The dynamic development of technology and construction of electrochemical capacitors (ECs), mostly driven by the needs of the automotive industry, leads to the conclusion that ECs are becoming a more viable alternative to traditional batteries. This is connected primarily with their ability to quickly charge and discharge, many times higher durability, maintenance-free operation and environment-friendly materials used for their production.

## Supercapacitors

Electrical energy can be chemically accumulated by Faradaic or non-Faradaic processes. In the first ones, charging and recharging of electrochemically active substances take place by reversible reactions of oxidation and reduction (the process requires electron transfer between electrode and electrolyte). In the second ones, storage and release of energy is based only on electrostatic separation of charge [1].

The most widely known energy storage devices are galvanic cells, commonly called batteries. The mechanism of energy accumulation in these devices is based on Faradaic processes. However, electrochemical capacitors, also called supercapacitors, become more and more popular in the energy market. ECs are comprised of two electrodes of high surface area. The electrodes are immersed in the electrolyte and separated by ion-selective membrane. Energy accumulation in supercapacitors is based mainly on physical, electrostatic and reversible adsorption of ions (coming from electrolyte) on electrodes (Fig. 1). Polarization of the electrodes results in formation of so-called electric double layer on both electrodes. In this case, capacitors accumulate energy only by electrostatic forces, and they are called Electrical Double-Layer Capacitors (EDLCs). In EDLCs electrodes are composed of carbonaceous materials.

Corresponding author:
Anna DETTLAFF – M.Sc., e-mail: anna.dettlaff@pg.gda.pl

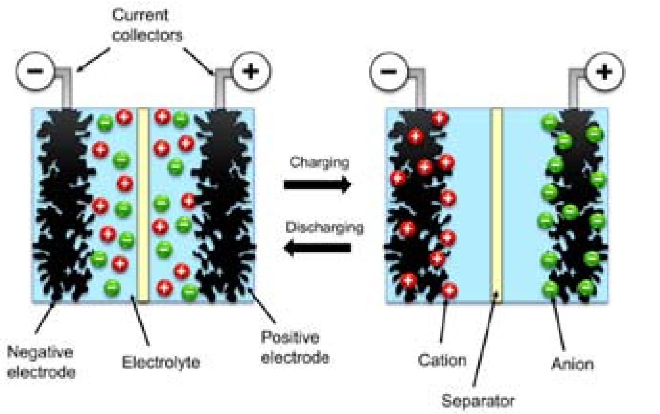


**Fig. 1. The operating principle of Electrical Double-Layer Capacitors**

The second type of electrochemical capacitors, beside using electrical double layer, accumulate energy by Faradaic processes and they are called pseudocapacitors. These devices utilize electrode materials showing so-called redox pseudocapacitance. Pseudocapacitance is a Faradaic process, which occurs mainly on a surface of electrode material and in a wide potential range [1]. Pseudocapacitive electrode materials exhibit the ability of fast and reversible redox reactions. The most common pseudocapacitive materials are transition metal oxides (e.g. ruthenium oxide) and electroactive polymers. It should be noted, however, that there are no supercapacitors, which use only pseudocapacitance or only electrical double-layer effect for accumulation of energy. The names of these capacitors originate from their main way of energy storage.

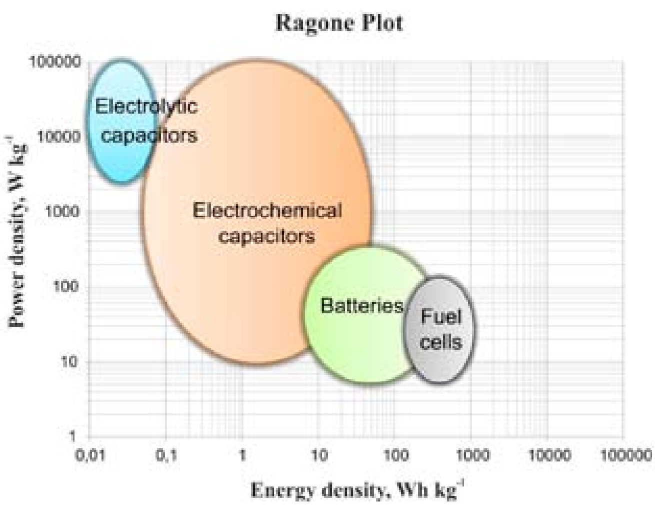


**Fig. 2. Ragone plot showing energy *vs.* power densities of selected power devices [2, 3].**

Despite the fact that supercapacitors and batteries have the same function and construction, they differ significantly. Supercapacitors can be fully charged and discharged in seconds. On the other hand, batteries need much longer time to charge, which is connected with the time of electrode reaction and much higher value of energy density that battery can store (~10 – 140 Wh $kg^{-1}$ for the batteries; ~0,1 – 20 Wh $kg^{-1}$ for the supercapacitors). ECs, by contrast, show greater power density (even $10^5$ W $kg^{-1}$ compared to ~150 W $kg^{-1}$ for batteries) (Fig. 2.). Hence, the supercapacitors can receive and deliver, in a very short time, pulses of high power.

Furthermore, EDLCs exhibit unlimited reversibility due to physical interactions between electrodes and electrolyte (they can be charged and discharged even million times). In batteries, the electron transfer and changing of the oxidation state of electrode materials, often connected with phase transition, results in side reactions and consumption of chemical reagents. Thus, cyclability in batteries is limited to several thousand.

**Storage of renewable energy using supercapacitors**

The amount of electrical energy generated from renewable sources by wind farms or photovoltaic cells is constantly changing, due to the variable weather conditions. This applies particularly to photovoltaic systems that can generate energy only during those hours, when sunlight reaches them.

The daily period (the time from sunrise to sunset) includes for Poland over 51% of the 8767 hours in an average year, and the northern region has this period longer by 24 hours than the southern one. During winter time, the southern Polish borders have a day longer by almost 1 hour compared to the north part, while in the summer the situation is opposite. In June the daylight hours in the north include 71.5% of the hours of the whole month, whereas in the central and the south regions it is 69% and 67%, respectively. In December, the situation changes and in the north part daylight hours are only 29.5%, while in the centre and in the south it is 31.7% and 34.7%, respectively.

This variation causes a number of problems for the stand-alone installations, as well as for the ones connected to the grid, which require the usage of a buffer energy storage system. Supercapacitors may become an alternative to traditional batteries, unfortunately, due to their high price – an expensive one. However, the number of charging and discharging cycles of supercapacitors declared by manufacturers is by 400 to 1000 times higher than number of cycles for batteries. Thus, the cost of installation consisting of batteries of the same cyclability as supercapacitors is 16 to 40 times higher. Therefore, it is advisable to use the supercapacitors in renewable energy power plants due to the durability and reliability of the installation and the wide range of operating temperatures. Moreover, supercapacitors are more suitable than batteries for rapid and frequent charging and discharging with high currents.

**Experimental part**

In this work, synthesis of nanocomposites based on multi-walled carbon nanotubes – MWCNTs (electrical double-layer material) and conducting polymer: poly(3,4-ethylenedioxythiophene) – pEDOT (pseudocapacitive character) was carried out. Carbon nanotubes (CNTs) are characterised by: high surface area (about 200 $m^2$ $g^{-1}$) [4], mechanical strength, good electrical conductivity and chemical stability [4, 5]. However, they exhibit insufficient electrical capacitance compared to the other carbonaceous materials of higher surface area. Electroactive polymers, in turn, show high value of the density of electric charge [6], significant value of the specific capacitance [7] and high electrical conductivity in the conductive state (~100 – 10000 S $m^{-1}$) [8]. Moreover, they create very good conducting matrix for different kind of composite materials [9 – 12] and they can be obtained directly on electrode, which allows to eliminate the addition of a binder.

Unmodified carbon nanotubes are strongly hydrophobic, which hinders their uniform dispersion in polar solvents [13]. The increase of hydrophilicity of carbon nanotubes can be obtained by: *i)* non-covalent functionalization by addition of the surfactants, nucleic acids or polymers, which adsorb on the surface of CNTs and facilitate their separation [14 – 16], *ii)* covalent functionalization by attachment of functional groups by chemical reaction e.g. oxidation or reaction with nitrogen compounds [17 – 21].

In this study MWCNTs were modified in both ways. The covalent functionalization was carried out by introduction of oxygen-rich groups (e.g. carboxyl moieties –COOH) on the carbon nanotubes surface by the acid treatment (65% nitric acid (V), 24 h, 121°C). The non-covalent modification was based on addition of the surfactant Triton X-100 (polyethylene glycol *tert*-octylphenyl ether – TrX) to the aqueous suspension of carbon nanotubes and sonication for 30 hours.

The synthesis of the nanocomposite consisting of modified multi-walled carbon nanotubes (COOH-MWCNTs and MWCNTs/TrX) and electroactive polymer (pEDOT), was carried out electrochemically. It was based on the potentiostatic electropolymerisation from the aqueous suspension of CNTs with monomer (EDOT) and electrolyte poly(sodium 4-styrenesulfonate) (PSS). The layers of nanocomposites (pEDOT/COOH-MWCNTs/PSS and pEDOT/MWCNTs/TrX/PSS) were electrodeposited directly on the electrode substrate [22].

The obtained electrode layers were investigated electrochemically by multicyclic galvanostatic ($j$ = 0.25 mA $cm^{-2}$) charging and discharging in order to determine their electrical capacitance and stability. The results show that the higher capacitance values, compared to the pure polymer, are achieved by nanocomposite containing chemically modified carbon nanotubes with oxygen functional groups. The non-covalent functionalization, in turn, does not bring about the expected effects – the electrical capacitance is not higher than for pure polymer, probably due to the insufficient homogeneity of the pEDOT/MWCNTs/TrX/PSS nanocomposite layers. As presented in the Figure 3, the nanocomposite layer (pEDOT/COOH-MWCNTs/PSS) exhibits the capacitance value equal to about 124 F $cm^{-3}$, while the pure polymer (pEDOT/PSS) achieves volumetric capacitance of about 90 F $cm^{-3}$. Furthermore, the layer with carbon nanotubes exhibits slightly better stability over multiple charge-discharge cycles. After 1000 cycles the nanocomposite layer (pEDOT/COOH-MWCNTs/PSS) retains 85% of the initial capacitance whereas the pure polymer only 76% .

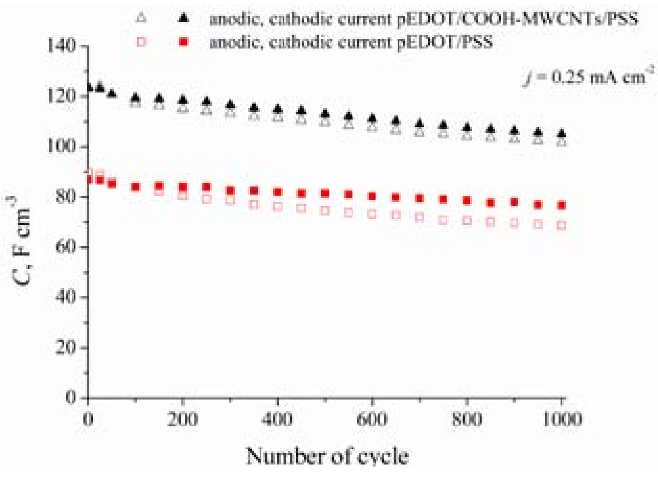


**Fig. 3. Volumetric electrical capacitance as a function of number of charge-discharge cycles obtained for pure polymer (pEDOT/PSS) and nanocomposite (pEDOT/COOH-MWCNTs/PSS); electrolyte: 0.1 M $Na_2SO_4$**

The presented studies show the importance of proper design of new electrode materials. It is worth noting that not only physicochemical properties of individual components are important, but also their appropriate combination. The inhomogeneity of the composite may results in the deterioration of the electrochemical properties compared to the pure components.

The application possibility of the commercial supercapacitor modules in the photovoltaic systems was investigated [23]. The experiments were carried out by using 4 modules of the supercapacitors. The type of electrochemical capacitor was BMOD0500 P016 B01 500 F/16 V. By combining these modules in parallel, a battery with a capacitance of 2000 F/16 V is received, and by series connection the capacitance is equal to 125 F/64 V, and by series-parallel connection 500 F/32 V. The next step was the study of the battery comprising of four modules connected in series-parallel way with capacitance: 500 F/32 V. The experimental set-up was equipped with the DC power supply type 6012 A, 0 – 60 V/0 – 50 A, 1000W, programmable 600 W DC electronic load type 8510, allowing the removal characteristics under constant current, constant voltage, constant power and constant resistance and the multimeter equipped with a universal 20-channel multiplexer card type Keithley 7700.

The curve of the self-discharge and the charging-discharging characteristic of the supercapacitor battery under constant charge and discharge current (equal to 10 A) were determined. On the basis of these measurements the capacitance of the battery was calculated. It is equal to 4 Ah and is consistent with the calculated theoretical value.

In certain applications, it is necessary to install equipment in the DC/DC converter, which is able to convert, the varying over a wide range, input voltage, to the constant output voltage. Different converters based on systems: LM 5118, LM 25118, LTC 3789 and TPS 40200 were designed, manufactured and tested. The converters were built based on monolithic integrated circuits type LM 25118 and LTC 3789. The LM 25118 type allows on the changing of input voltage from the range of 5 – 42 V to the output voltage of any value in the range of 1.23 – 38 V. The LM 25118 system equipped with the synchronizing output enables the parallel work to five converters, which, in turn, allows to increase the output current to the value of 15 A. The LTC 3789 system allows for stabilization of voltage to any value in the range 0.8 – 38 V and to obtain the maximum output current of 12 A.

The range of the operating temperature values (of the both converters) corresponds well with the range of the operating temperatures of the supercapacitors system.

**Conclusions**

Supercapacitors can be a very good source of electrical energy storage in renewable energy power plants. The important parameter of the electrochemical capacitors is their specific and volumetric electrical capacitance, which may be increased through the use of new, improved electrode materials with a high energy density and stability during the multicyclic charging and discharging processes. The design of new composite materials requires not only a proper choice of the relevant components, but also the optimal combination of these components. Both parameters ensure homogeneity and reproducibility of the final composite material. There is a need for further investigations to obtain new electrode materials and electrolytes in order to increase the electrical capacitance values and to improve the operating parameters of supercapacitors such as energy density or operating voltage window.

**Acknowledgements**

The financial support from Norway Grants in the Polish-Norwegian Research Programme (Small Grant Scheme) operated by the National Centre for Research and Development, grant No. POL-NOR/209673/9/2013 entitled „Nanocomposites based on conducting polymers and carbon materials for supercapacitor application" is gratefully acknowledged.

**Literature**


1. Conway B. E.: Electrochemical supercapacitors. Scientific fundamentals and technological applications., New York, 1999.
2. Yu G., Xie X., Pan L., Bao Z., Cui Y.: Hybrid nanostructured materials for high-performance electrochemical capacitors, Nano Energy 2013, **2**, 2, 213–234.
3. Holmberg S., Perebikovsky A., Kulinsky L., Madou M.: 3-D Micro and Nano Technologies for Improvements in Electrochemical Power Devices, Micromachines, 2014, **5**, 2, 171–203.
4. Bai X., Hu X., Zhou S., Yan J., Sun C., Chen P., Li L.: In situ polymerization and characterization of grafted poly (3,4-ethylenedioxythiophene)/multiwalled carbon nanotubes composite with high electrochemical performances, Electrochimica Acta 2013, **87**, 394–400.
5. Merkoçi A., Pumera M., Llopis X., Pérez B., del Valle M., Alegret S.: New materials for electrochemical sensing VI: Carbon nanotubes, Trends in Analytical Chemistry 2005, **24**, 9, 826–838.
6. Snook G. A., Kao P., Best A. S.: Conducting-polymer-based supercapacitor devices and electrodes, Journal of Power Sources 2011, **196**, 1, 1–12.
7. Chen W., Xia C., Rakhi R. B., Alshareef H. N.: A general approach toward enhancement of pseudocapacitive performance of conducting polymers by redox-active electrolytes, Journal of Power Sources 2014, **267**, 521–526.
8. Liu T., Finn L., Yu M., Wang H., Zhai T., Lu X., Tong Y., Li Y.: Polyaniline and polypyrrole pseudocapacitor electrodes with excellent cycling stability., Nano letters 2014, **14**, 5, 2522–7.
9. Wilamowska M., Lisowska-Oleksiak A.: Hybrid electrodes composed of electroactive polymer and metal hexacyanoferrates in aprotic electrolytes, Journal of Power Sources 2009, **194**, 1, 112–117.
10. Wilamowska M., Lisowska-Oleksiak A.: Synthesis and electrochemical characterization of poly(3,4-ethylenedioxythiophene) modified by iron hexacyanocobaltate, Solid State Ionics 2011, **188**, 1, 118–123.
11. Reddy B. N., Deepa M., Joshi A. G.: Highly conductive poly(3,4-ethylenedioxypyrrole) and poly(3,4-ethylenedioxythiophene) enwrapped $Sb_2S_3$ nanorods for flexible supercapacitors., Physical chemistry chemical physics 2014, **16**, 5, 2062–71.
12. Ranjusha R., Sajesh K. M., Roshny S., Lakshmi V., Anjali P., Sonia T. S., Sreekumaran N. A., Subramanian K. R. V.: Supercapacitors based on freeze dried $MnO_2$ embedded PEDOT: PSS hybrid sponges, Microporous and Mesoporous Materials 2014, **186**, 30–36.
13. Moore J. J., Kang J. H., Wen J. Z.: Fabrication and characterization of single walled nanotube supercapacitor electrodes with uniform pores using electrophoretic deposition, Materials Chemistry and Physics 2012, **134**, 1, 68–73.
14. Jin S. H., Cha S. I., Jun G. H., Oh J. Y., Jeon S., Hong S. H.: Non-covalently functionalized single walled carbon nanotube/poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) nanocomposites for organic photovoltaic cell, Synthetic Metals 2013, **181**, 92–97.
15. Klumpp C., Kostarelos K., Prato M., Bianco A.: Functionalized carbon nanotubes as emerging nanovectors for the delivery of therapeutics, Biochimica et Biophysica Acta 2006, **1758**, 404–412.
16. Chehimi M. M., Pinson J., Salmi Z.: Carbon nanotubes: surface modification and applications., Applied Surface Chemistry of Nanomaterials 2013, 95–143.
17. Rosca I. D., Watari F., Uo M., Akasaka T.: Oxidation of multiwalled carbon nanotubes by nitric acid, Carbon 2005, **43**, 3124–3131.
18. Datsyuk V., Kalyva M., Papagelis K., Parthenios J., Tasis D., Siokou A., Kallitsis, I., Galiotis, C.: Chemical oxidation of multiwalled carbon nanotubes, Carbon 2008, **46**, 833–840.
19. Basiuk E. V., Basiuk V. A., Meza-Laguna V., Contreras-Torres F. F., Martínez M., Rojas-Aguilar A., Salerno M., Zavala G., Falqui A., Brescia R.: Solvent-free covalent functionalization of multi-walled carbon nanotubes and nanodiamond with diamines: Looking for cross-linking effects, Applied Surface Science 2012, **259**, 465–476.
20. Zhong C., Gong S., Jin L., Li P., Cao Q.: Preparation of nitrogen-doped pitch-based carbon materials for supercapacitors, Materials Letters 2015, **156**, 1–6.

21. Lin T., Bajpai V., Ji T., Dai L.: Chemistry of carbon nanotubes Australian Journal of Chemistry 2003, **56**, 7, 635–651.
22. Dettlaff A., Wilamowska M.: Electrochemical synthesis and characterization of nanocomposites based on poly(3,4-ethylenedioxythiophene) and functionalized carbon nanotubes, Synthetic Metals 2016, **212**, 31–43.
23. Grzesiak W., Maćków P., Piekarski J., Klugmann-Radziemska E., Grzesiak P.: Komercyjne moduły superkondensatorów. Wybrane zagadnienia aplikacyjne, Przegląd Elektrotechniczny 2013, **89**, 10, 80–82.



*Anna DETTLAFF – M.Sc., she is a Ph.D. student at the Faculty of Chemistry at the Gdansk University of Technology. In 2013, she received a Master of Science degree with honours. She works in a team engaged in the research of new composites serving to the energy storage devices. Research interests: supercapacitors, renewable energy sources. She is the author of 2. scientific papers published in reputable journals.
e-mail: anna.dettlaff@pg.gda.pl

Monika WILAMOWSKA-ZAWŁOCKA – Ph.D., (Eng.), she obtained her Ph.D. in Chemistry in 2011 at Faculty of Chemistry, Gdańsk University of Technology. She then was a post-doctoral fellow at Technische Universität Darmstadt, Germany. She has worked as an Assistant Professor at Gdańsk University of Technology since 2013. Her research interests include composite materials for energy storage devices, especially anodes for lithium-ion batteries and nanocomposites based on electroactive polymers for electrochemical capacitors.

Ewa KLUGMANN-RADZIEMSKA – Ph.D., D.Sc., Assoc. Prof., physician, she has graduated from University of Gdańsk. She has worked at Faculty of Chemistry, Gdańsk University of Technology since 1996, at the moment as an Associate Professor. She published over 270 scientific papers, is the author of several books and handbooks as well as 11 patents and patent applications. Recently she focused on the research devoted to influence of temperature on power decrease of silicon crystalline photovoltaic cells, recycling of PV cells and modules and the investigation of potential application of photovoltaic energy.
e-mail: ewa.klugmann-radziemska@pg.gda.pl


# Aktualności z firm

News from the Companies

*Dokończenie za strony 250*

## NOWE PRODUKTY

**LANXESS: trwałe kolory w przestrzeni miejskiej**

Na targach Bauma 2016 koncern LANXESS pokazała, że konwencjonalne materiały budowlane, takie jak barwione dachówki, ekrany akustyczne, wylewki betonowe na miejscu, płyty włóknistocementowe, cegły wapienno-piaskowe czy asfalt, mogą kolorystycznie ożywić przestrzeń. Wraz z dystrybutorem, spółką Harold Scholtz & Co. GmbH, producentem specjalistycznych środków chemicznych wystawił swoje pigmenty nieorganiczne klasy premium na jednych z najważniejszych międzynarodowych targów branży budowlanej w Monachium, od 11 do 17 kwietnia br.

*– Nasze pigmenty, charakteryzujące się stabilnym zabarwieniem i wysoką odpornością na warunki atmosferyczne, nadają trwały kolor elementom architektonicznym i infrastrukturze. Materiały budowlane zabarwione tymi produktami zachowują wygląd i walory estetyczne nawet przy długotrwałym narażeniu na działanie czynników pogodowych. Nie wymagają też praktycznie żadnej konserwacji* – mówi Thomas Pfeiffer, wiceprezes ds. marketingu i sprzedaży w regionie EMEA z jednostki biznesowej Inorganic Pigments. *– Zgodność z zasadami zrównoważonego rozwoju stanowi jeden z priorytetów w odniesieniu do wszystkich naszych produktów i procesów. Jest też nieodzownym elementem naszej filozofii biznesowej. Procesy produkcyjne we wszystkich naszych zakładach są zaprojektowane w taki sposób, aby były bezpieczne, oszczędne pod względem zasobów i przyjazne dla środowiska. (kk)*

*(Informacja prasowa LANXESS, 15.04.2016)*

**Nowy super ciepły Synthos XPS Prime D**

Strategicznym celem firmy Synthos jest innowacyjność w branży tworzyw termoizolacyjnych. Realizując te właśnie zadania, opracowane zostały czarne płyty XPS Prime D. Nowe, super ciepłe polistyreny ekstrudowane posiadają niespotykaną dotąd lambdę max 0,029, co jest wynikiem o 10% lepszym od pozostałych XPS dostępnych na rynku! *(abc)*

*(http://synthosgroup.com/media/informacje-prasowe/, 14. 04.2016)*

## NOWE INWESTYCJE

**Nowe Centrum Badawczo-Rozwojowe Grupy Adamed**

W Centrum Badawczo-Rozwojowym Grupy Adamed opracowywane są leki generyczne i innowacyjne, z wykorzystaniem najnowszych osiągnięć syntezy organicznej oraz technologii i formulacji stałych postaci leków. Centrum poprowadzi projekty w fazie laboratoryjnej, będącej podstawą do wdrożenia szerszej produkcji przez zakłady Grupy Adamed. Inwestycja umożliwia m.in. opracowywanie leków na podstawie zaawansowanej technologii Hot Melt Extrusion (HME), zapewniającej lepszą biodostępność substancji leczniczej oraz mniej działań niepożądanych w stosunku do tradycyjnych form leków. W laboratoriach prowadzone są też intensywne badania nad otrzymaniem nowych molekuł – potencjalnych leków o zastosowaniach w różnych obszarach terapeutycznych. Wykorzystywanie najnowszych technik analitycznych, zgodność z aktualnymi wymaganiami europejskimi oraz wysoce specjalistyczna wiedza wykorzystywana podczas rozwoju nowych produktów umożliwia uzyskiwanie pozwoleń na dopuszczenie do obrotu na rynkach światowych. *(kk)*

*(http://adamed.com.pl/, 21.04.2016)*

## KONKURSY, NAGRODY, WYRÓŻNIENIA

**SYNTHOS CHEMICAL AWARD – milion złotych dla najlepszego polskiego chemika**

Synthos SA, europejski lider w produkcji kauczuków syntetycznych oraz polistyrenów do spieniania EPS, ogłasza konkurs dla naukowców – badaczy w obszarze chemii. Kapituła Konkursu, w której skład wchodzą wybitni polscy chemicy, wybierze osobę, która za swoje odkrycia naukowe otrzyma nagrodę w wysokości 1 miliona złotych! To pierwszy w historii polskiej nauki konkurs, w którym do wygrania jest taka kwota. Zgłoszenia do Synthos Chemical Award będą przyjmowane już od 1 maja br.(więcej informacji o Synthos Chemical Award na str. 281). *(abc)*

*(http://synthosgroup.com/media/informacje-prasowe/, 27. 04.2016)*

*Dokończenie na stronie 265*