Workshop in Bucharest, September 17-18, 2008
National Research Institute for Electrical Engineering
(INCDIE ICPE-CA)

Development of Promised Materials for Electrochemical Power Engineering.

State of Art and Perspectives on Hydrogen and Fuel Cells Research in Ukraine.

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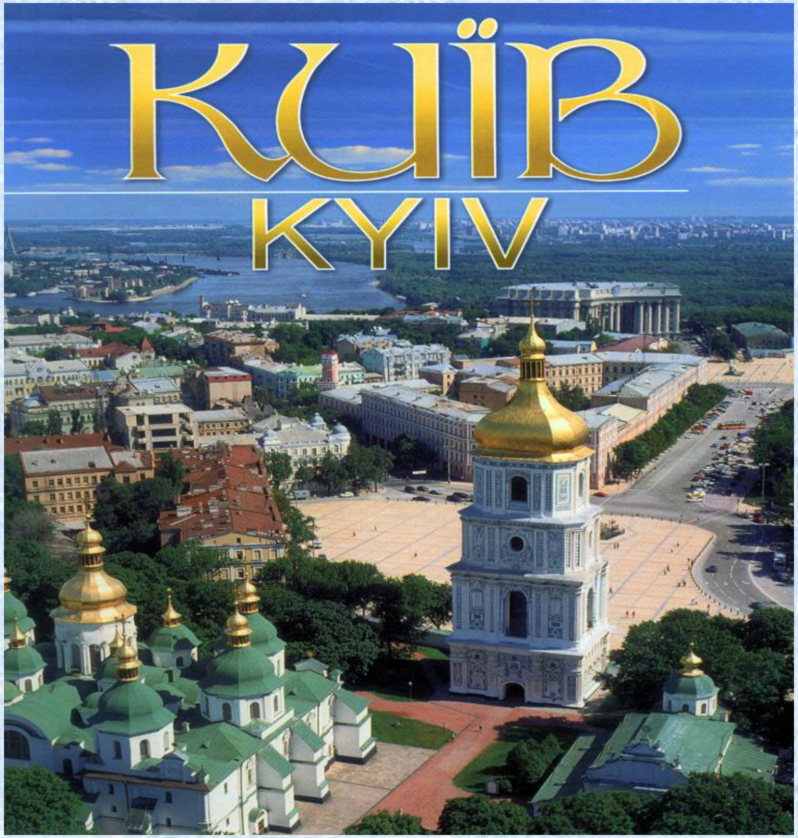
Outline

Part 1. State of the Art for Hydrogen and Fuel Cells Research in Ukraine:

- *Historical aspect*
- *Modern Directions of R&D*
- *Main R&D and Industrial Centers in the Field*
- *International Cooperation, etc.*
- *Conclusion-1*

Part 2. Development of Novel Inexpensive Catalysts in KNUTD:

- *Conducting Polymers based Catalysts for Oxygen Reduction*
- *Amorphous Oxides of Transition Metals (like MnO_2)*
- *Novel Carbon Supports for Composite Catalysts*
- *Conclusion-2*



Ukraine is a traditional center for R&D in the field of Fuel Cells and Batteries since 1950-60:

Prof. Ksenzhek - theory of porous gas-diffusion electrodes;

Prof. Davtyan – first model of H_2-O_2 AFC in Odessa State Univ.;

Prof. Koshel - model of Hydrazine - H_2O_2 FC in DnCh-Tech. Univ.

The Modern Directions of R&D in Ukraine

- HYDROGEN SYNTHESIS & STORAGE (Electrochemical, Photochemical, Chemical methods of synthesis, Metal Hydrides, Carbon Nanostructural Materials, etc.)
- CATALYSTS FOR FUEL CELLS (Novel Non-Noble Catalysts, Reducing the Noble Catalysts Content, Carbon Nanostructural Supports, etc.)
- GAS-DIFFUSION ELECTRODES (Theory, Construction, Technologies)
- FUEL CELLS MODELS (PEM, AFC, MCFC, SOFC, etc.)
- Semi-FUEL CELLS/Hybrid BATTERIES (Air-Metal Batteries, Ni-MH Batteries, Hybrid FC-Battery Systems of Power Engineering)
- FIRE AND EXPLOSION SAFETY OF HYDROGEN-CONTAINING MATERIALS AND DEVICES
- HYDROGEN ENERGY AND ECOLOGICAL PROBLEMS

So, the directions of R&D include practically all main aspects of the ***Hydrogen Power Engineering and Fuel Cells Technology***

Main R&D and industrial centers in the field:

I. UNIVERSITIES:

- Kiev National University of Technologies & Design (non-noble catalysts for FCs, composite catalysts with novel carbon supports, gas-diffusion electrodes, Air-Metal batteries)
- National Technical University of Ukraine “Kiev Polytechnic Institute” (hydrogen in aluminium, hydrogen storage alloys)
- Sevastopol National University of Nuclear Energy & Industry (hydrogen fire & explosion safety)
- Ukrainian State Chemical-Technological University, Dniepropetrovsk (theory and models of gas-diffusion electrodes)
- Odessa State University (Air-Mg batteries)
- Lviv National University (hydrogen storage alloys)
- Dniepropetrovsk State University (Borohydrides of metals for hydrogen production)
- Chernigov State University of Technology (ecology safety)
- Ukrainian State Maritime University, Nikolaev (ecology safety)
- East Ukrainian National University, Lugansk (hydrogen corrosion)

II. Institutes of Ukrainian National Academy of Sciences (UNAS):

- Institute for Problems of Materials Science, Kiev (hydrogen storage in carbon nanomaterials, $LaNi_5$ based alloys, SOFC-materials and cells)
- Institute of Hydrogen and Solar Energy, Kiev (photovoltaic systems, wind energy systems, hydrogen power engineering)
- Donetsk Physical&Technical Institute (ZrO2 electrolytes doped with oxides metals)
- Institute of Thermal Physics, Kiev (environment safety)
- Institute of Physical Chemistry, Kiev (photochemical processes for hydrogen synthesis)
- Paton Institute of Electric Welding, Kiev (photochemical processes for hydrogen synthesis)
- Institute of General and Inorganic Chemistry, Kiev (electrochemical processes for hydrogen synthesis)

- Institute of Semiconductor Physics, Kiev (nanocomposites with carbon nanotubes)
- Institute for Metal Physics, Kiev (hydrogen storage in different materials)
- Institute of Physics (intercalation of InSe and GaSe layered crystals with hydrogen, hydrogen sensors for fire & explosion safety)
- National Scientific Center "Kharkov Institute for Physics and Technology" (mechano-chemical synthesis of Mg-Co hydrogen absorbing phases)
- Institute of Mechanical Engineering Problems, Kharkov (hydride-forming materials)
- Physic-Mechanical Institute, Lvov (hydrogen storage R-Mg-M systems: R-rare earth; M – transition metals)
- Institute for Machine Building Problems, Kharkov ($LaNi_5$–H_2/D_2 systems)

III. Industrial plants & companies

- State enterprise "Zirconium", Dnieprodzerjinsk (**Zirconium oxide production**)
- TM Spetsmash Ltd., Kiev (**MWNT production**)
- Association "UkrBATT", Lugansk (alkaline batteries for transport, **Ni-MH batteries** experimental production)
- State enterprise "Generator Plant", Kiev (Missile Electronic plant, **Li batteries, Air-Zn batteries** experimental production - potential end-user)
- Association "Batteries of Ukraine", Kiev (5 battery plants & 15 attendant companies - potential end-users)
- State enterprise "Yuzhmash" /"South machine works"/ (Missile plant, Renewable Energy Devices, in particular, **wind turbine generators** - potential end-user)

International Cooperation with the Following Main Institutions:

- International Association for Hydrogen Energy, USA
- Clean Energy Research Institute, USA
- International Energy Foundation, Canada
- International Center for Hydrogen Energy Technology (UNIDO), Turkey
- Institute of Physical Chemistry of PAS, Poland
- University of Miami, USA
- Florida Solar Energy Center, USA
- Aristotel University, Thessaloniki, Greece
- National Research Institute for Electrical Engineering, Bucharest, Romania
- Ecole Polytechnique de Montreal, Canada
- Inst. de Quimica de Sao Carlos, Universidade de Sao Paulo, Brasil
- Central Laboratory for Solar Energy and New Energy Sources, Sofia, Bulgaria
- Delft University of Technology, Delft, Netherlands
- Institute for Energy Technology, Kjeller, Norway
- Institute of Chemical Physics, Yerevan, Armenia
- Belarusian State University, Minsk, Belarus
- Institute of Solid State Physics of RAS, Chernogolovka, Russia
- Russian Research Center "Kurchatov Institute", Moscow, Russia, etc., etc., etc.

The Funding Level, Associations, International Conferences in UA

- The funding level of R&D Projects in the field is of about EUR 10 millions by our estimation.
- Many organizations and scientists in Ukraine are united in the Ukrainian Association for Hydrogen Energy.
- International Conference "Hydrogen Materials Science and Chemistry of Carbon Nanomaterials" (ICHMS) in Crimea is organized each 2 years.
- It is planned that the next conference of this series will be organized in the 2009 in Crimea, Ukraine.

Conclusion-1

1. There are more than 30 Universities, Institutes of UNAS, Industrial enterprises and companies involved in the FC and Alternative Energy problem in Ukraine.
2. Practically all aspects of the problem are studying, but the main focus is concentrated on the development of promising materials for FC, which could make this technology more inexpensive and effective.
3. Ukrainian scientists have some international cooperation with R&D centers abroad on the different levels (informational, participation in the conferences and workshops, be-lateral research cooperation, etc.). Nevertheless, we have an interest for much more wide level of the international cooperation, including participation in joint R&D projects and programs, like FP7 and similar programs.
4. We are open for such cooperation, which is necessary for wide development of FC and Alternative Energy Technologies.

Part 2. Development of Novel Inexpensive Catalysts in KNUTD

- *Short Introduction about KNUTD*
- *Conducting Polymers based Catalysts for Oxygen Reduction*
- *Amorphous Oxides of Transition Metals (like MnO_2)*
- *Novel Carbon Supports for Composite Catalysts*
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Kiev National University of Technologies & Design "K N U T D"

KNUTD is a comparatively young higher school in Ukraine. Having separated from the Kiev Polytechnic Institute in 1930, KNUTD is presently a well known scientific and educational center in Ukraine and abroad.

The KNUTD has presently now more than 6.000 students, 7 faculties, and 32 departments. There are about 550 scientists and teachers in the staff, more than 150 post-graduate students and Ph.D. students.

Department of Electrochemical Power Engineering & Chemistry

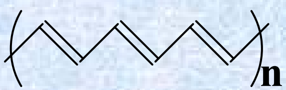
Department of Electrochemical Power Engineering & Chemistry is the only in Ukraine, which is specialized in educating the specialists in the field of Electrochemical Power Engineering and carry out corresponding R & D in these areas.

Department has 3 professors (Dr. Sci.), 10 docents (PhD), 7 young assistants and PhD students.

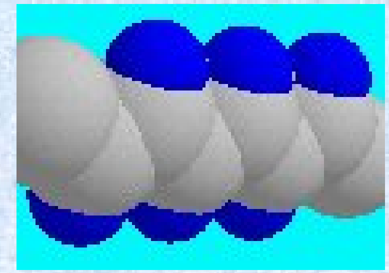
The main field of research interests – novel effective and not expensive active materials for modern batteries and fuel cells.

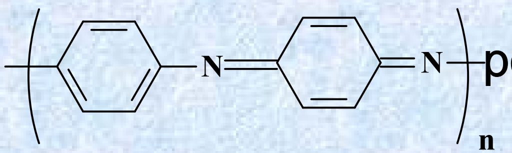
During the recent 5 years department was/is involved in the following international research programs: NATO SfP; EU (FP-6); IPP (US Department of Energy); CRDF; INTAS; be-lateral cooperation with Greece and Sweden.

Electronically conducting polymers (ECPs)

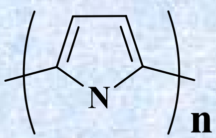


Polyacetylene (PA) is the prototype for other ECP

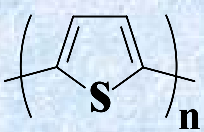




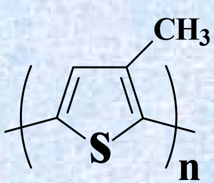
polyaniline (PANI)



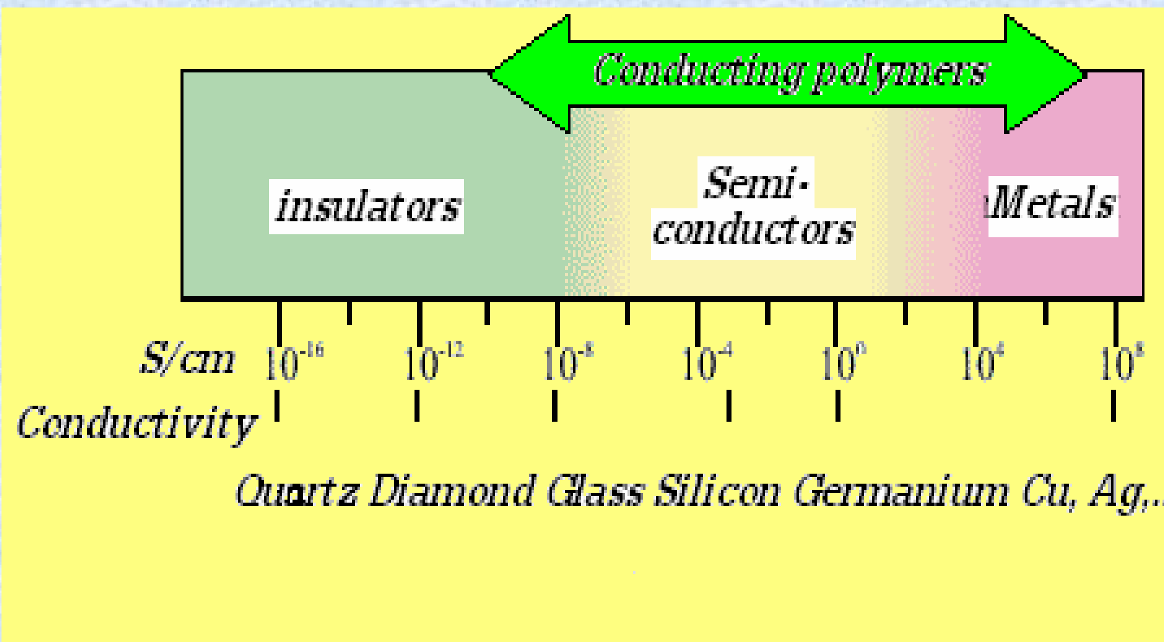
polypyrrole (PPy)

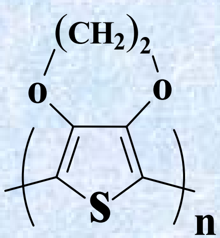


polythiophene (PT)



poly(3-methylthiophene) (PMeT)

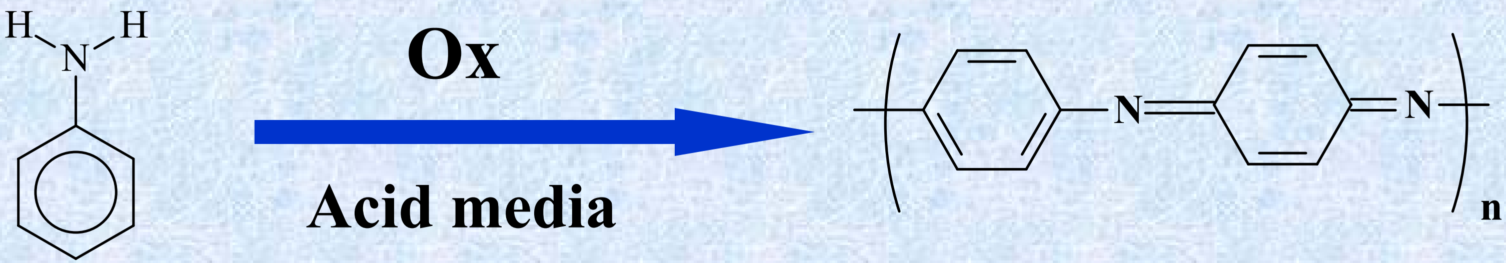




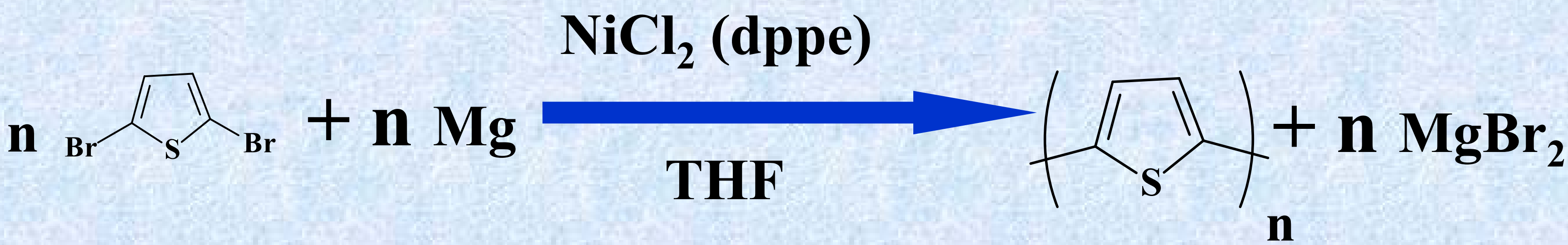
poly(3,4-ethylenedioxythiophene) (PEDOT)

Chemical synthesis of ECPs

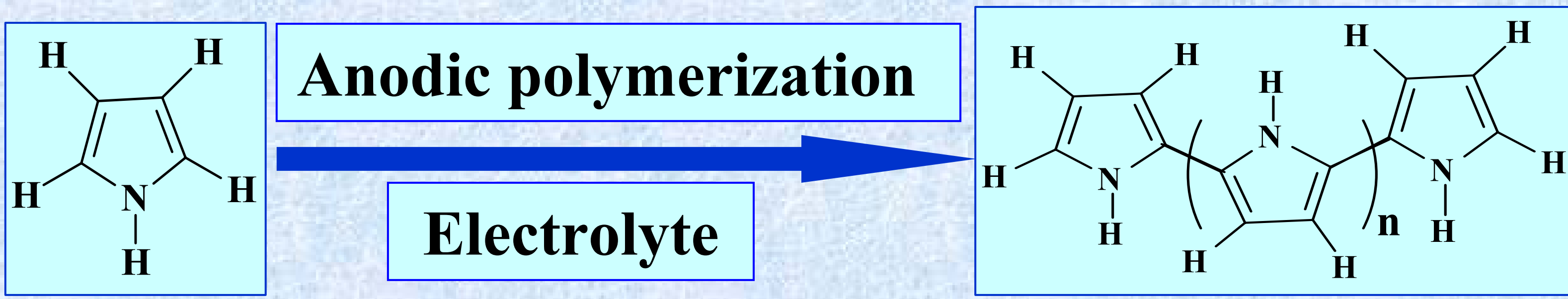
Oxidative polymerization of monomers by oxidant (Ox)



Synthesis by transition metal-catalyzed coupling the activated organometallic monomers



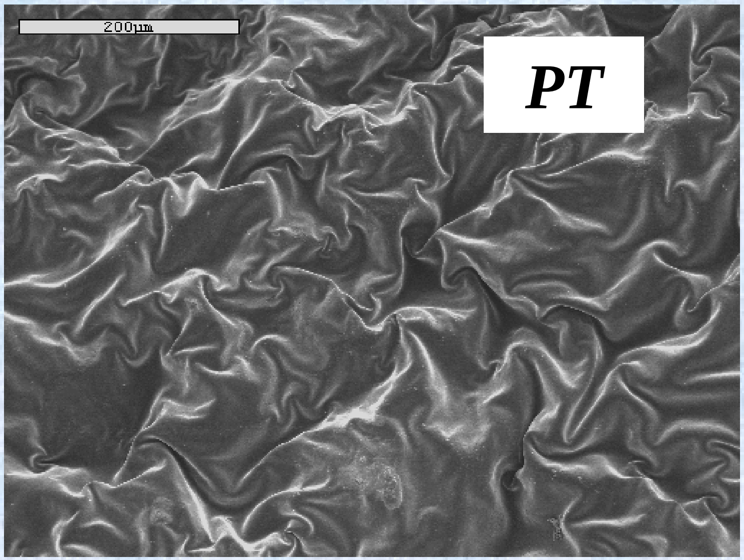
Electrochemical Synthesis

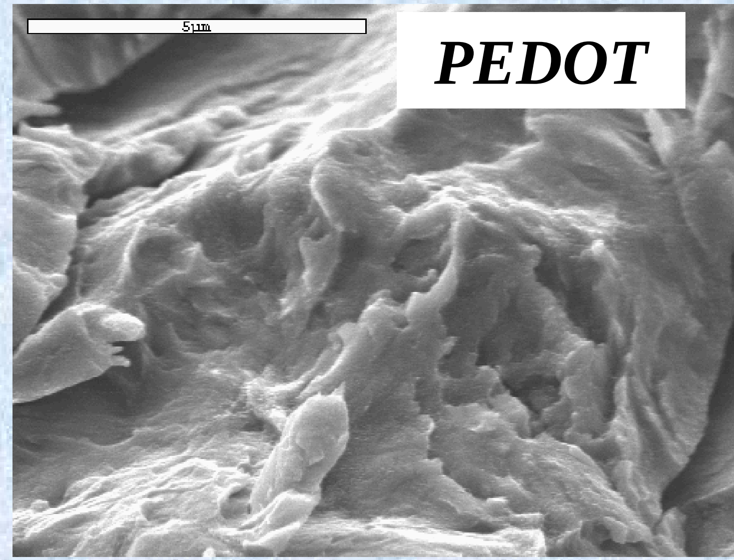


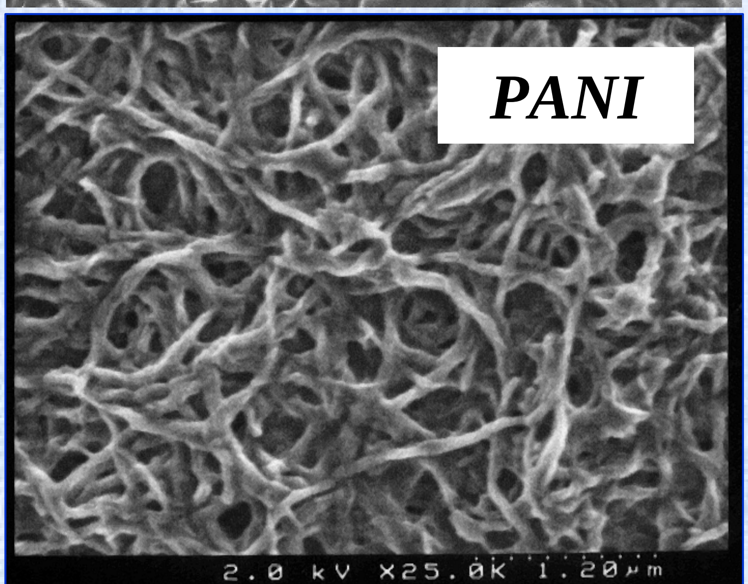
The anodic electrochemical synthesis ECP can be carried out by:

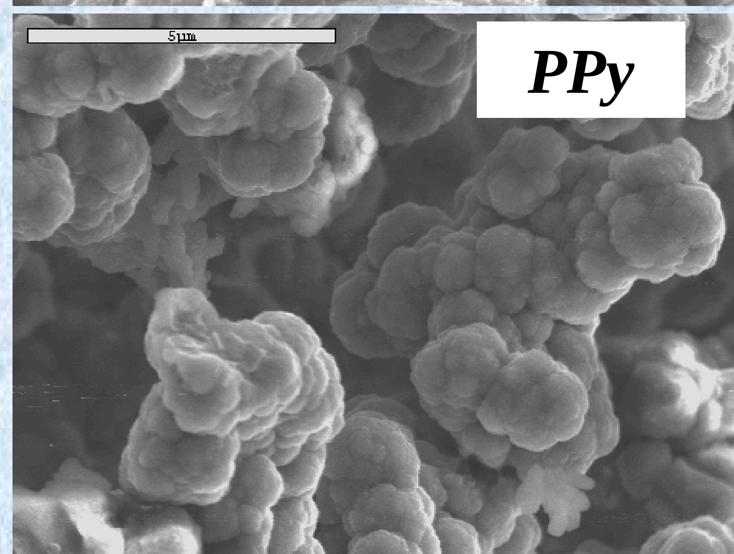
- **potentiostatically (E=const.)**
- **galvanostatically (I=const.)**
- **cyclic voltammetry**

Morphology of electronically conducting polymers

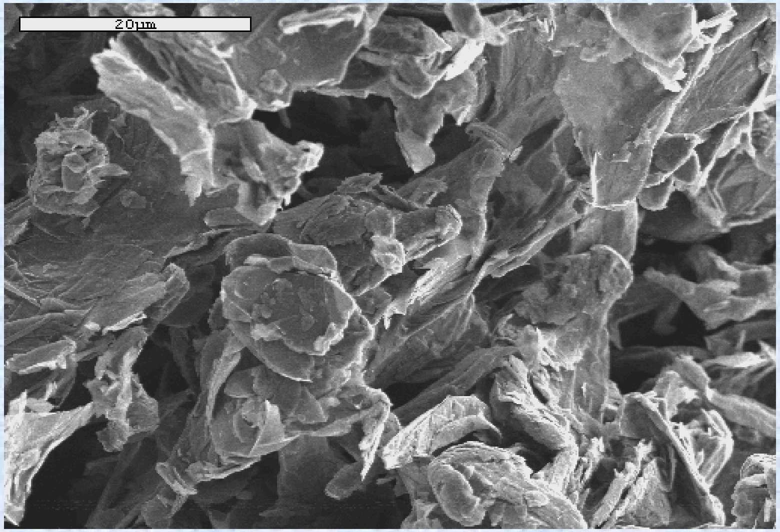




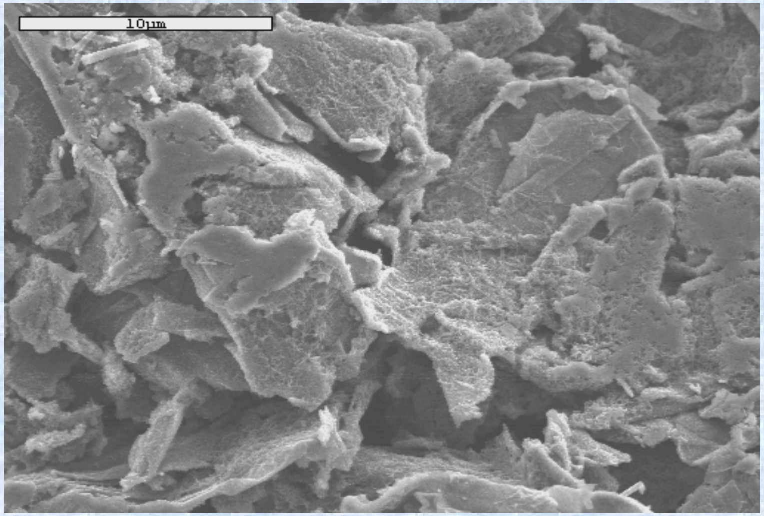


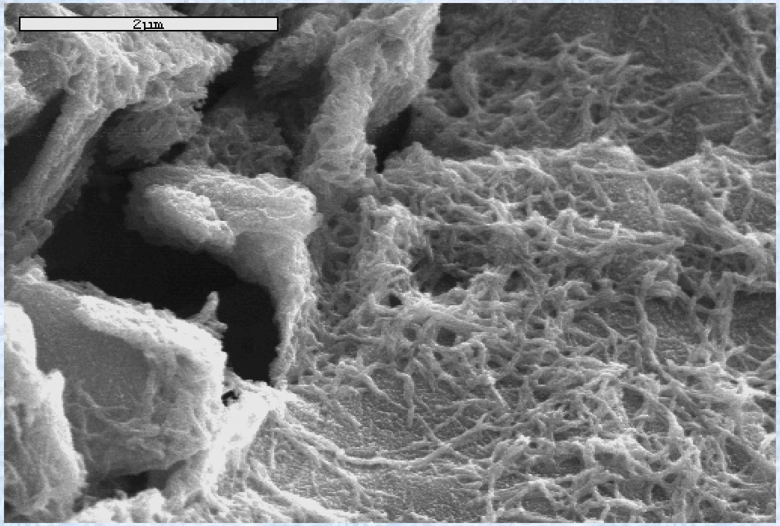


Morphology of composite materials based on PANI & thermally exfoliated graphite (TEG)



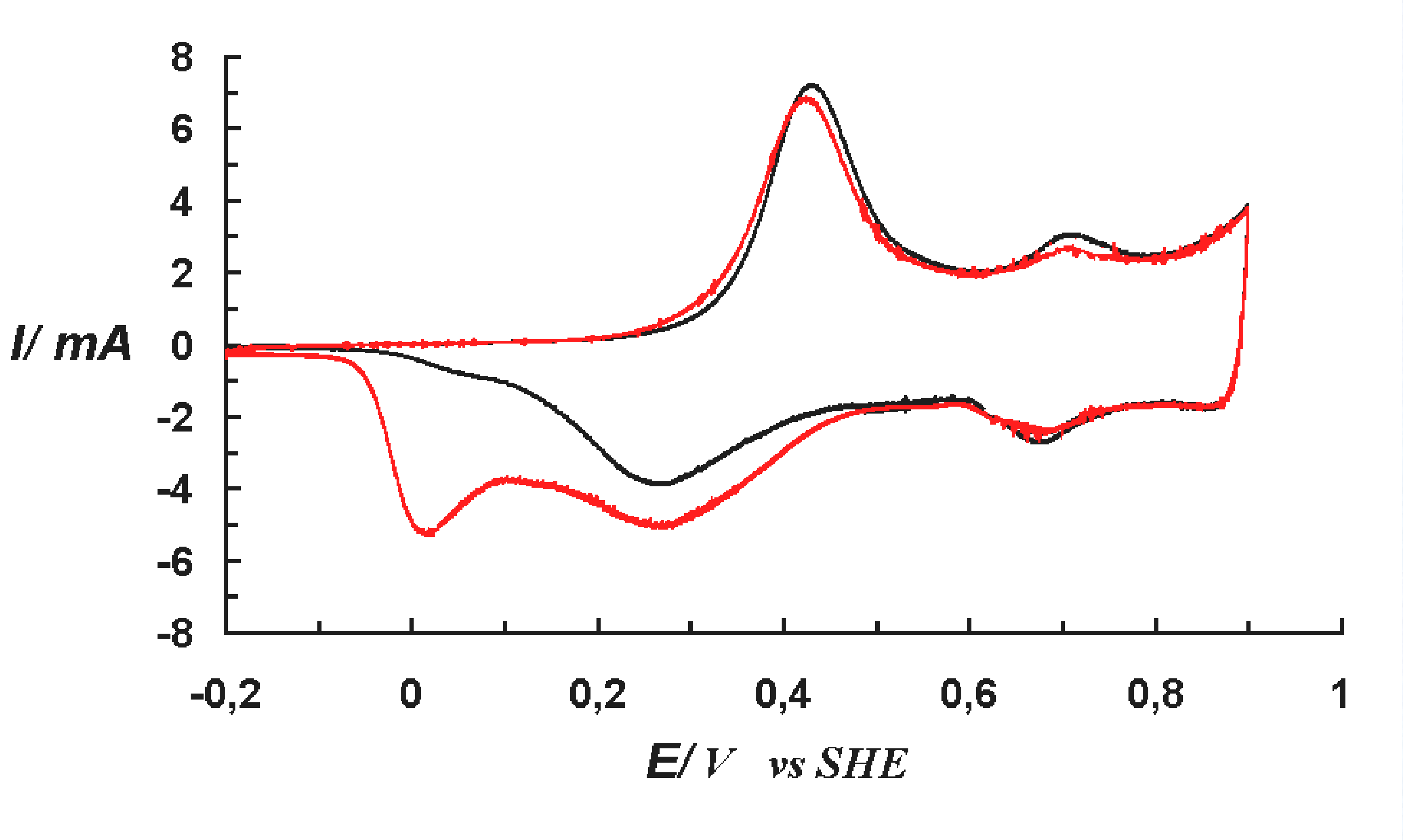
SEM's micrographs of TEG before polymerization of PANI



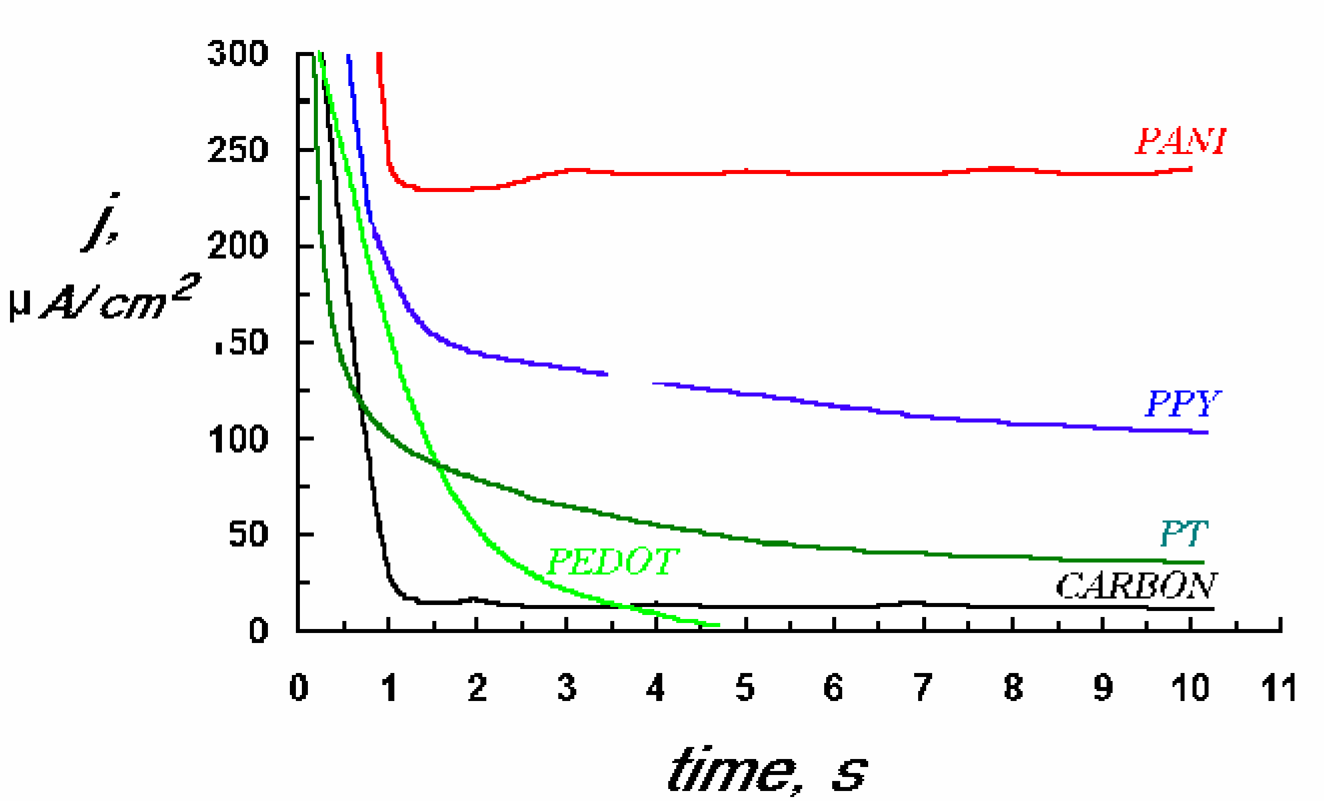


Cyclic voltammetry of catalytic electrode based on PANI in oxygen (red line) and nitrogen (black line)

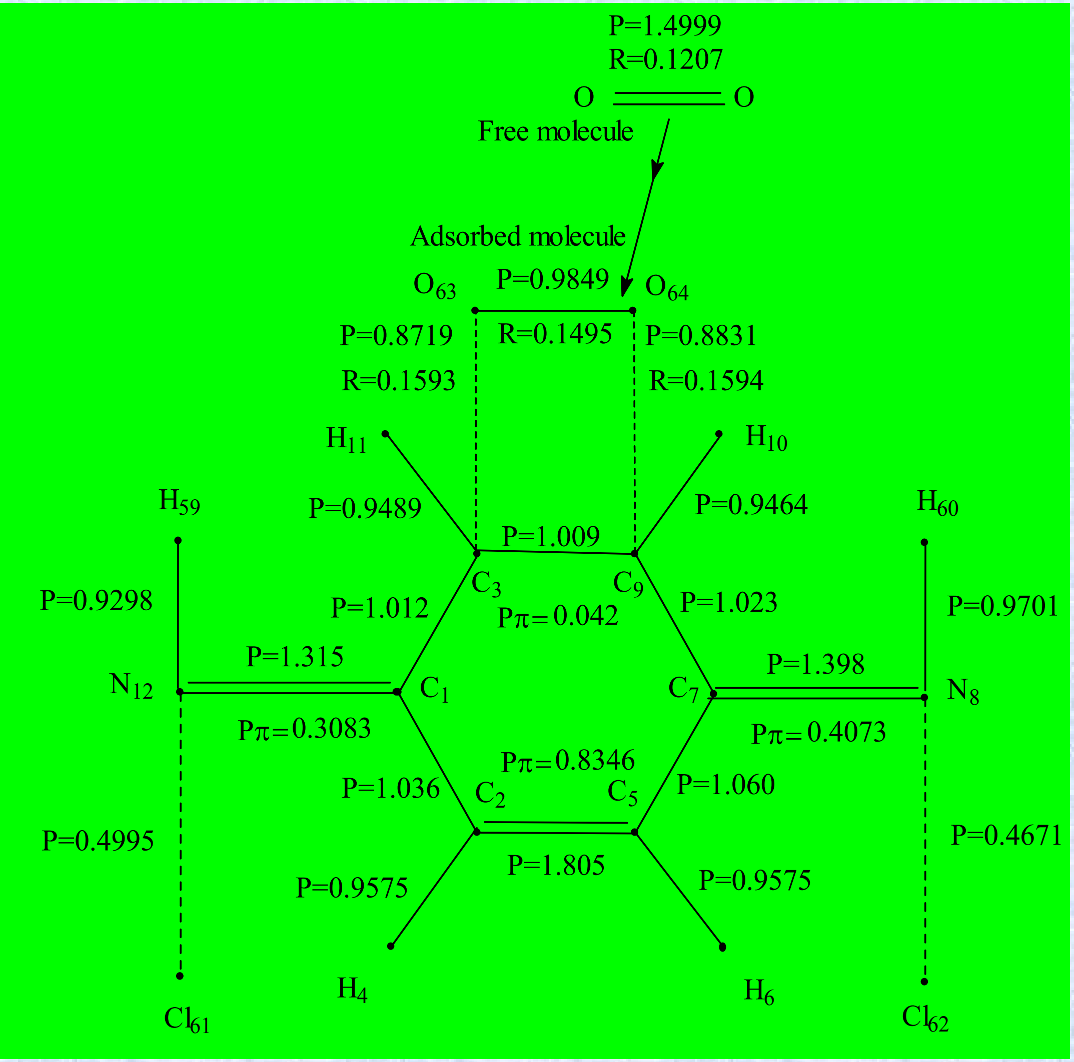
saturated 1 M HCl solution at scan rate 2 mV/s



I-t response of CPs electrodes (m=0.6 mg, ∅5-mm) in oxygen saturated 1M HCl. The electrodes were polarized by stepped ΔE from 0.6 to 0.0V

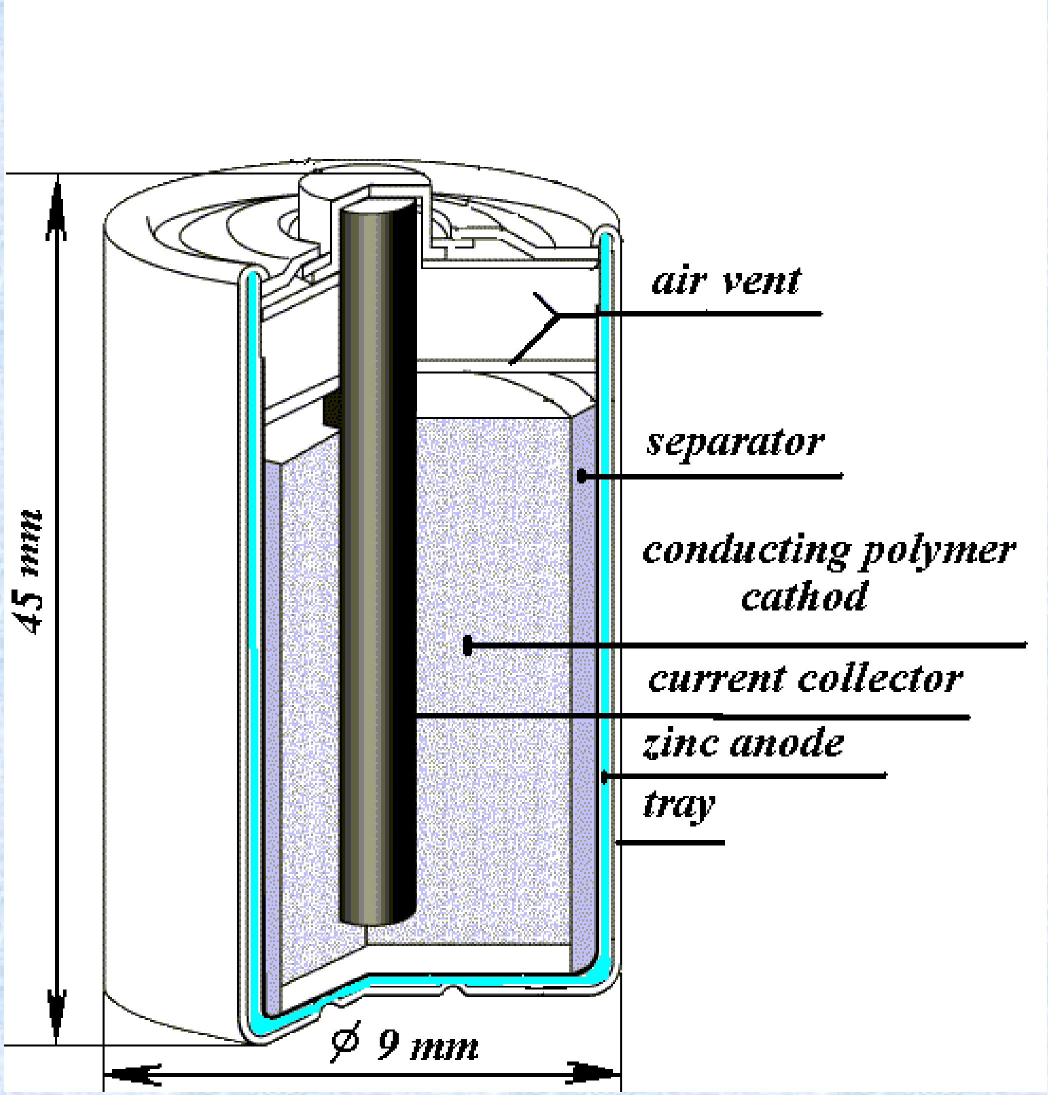


The results of quantum-chemical calculations for doped "PAN-O_2" molecular complex (fragment of cluster)

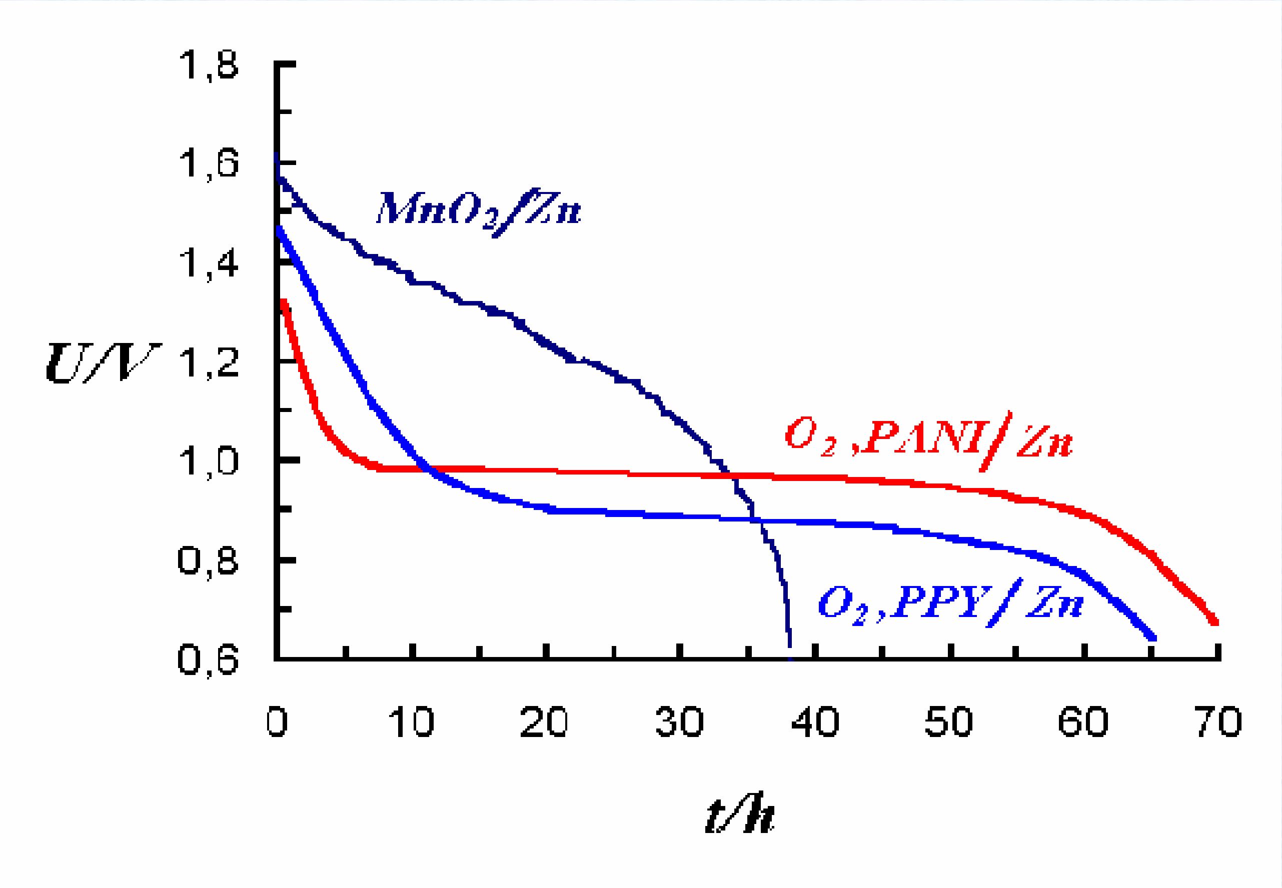


Calculations show that the 0-0 bond orders in the chemisorbed oxygen molecules are almost of 30 % lower than those in a free O_2 molecule. Besides, a noticeable increase (of more than 20 %) in O-O bond length takes place during the chemical adsorption. Thus, chemisorbed O_2 molecules have a fairly high degree of activation and can be easily reduced, what can explain a catalytic activity of PANI.

Schematic configuration of AAA size Air-Zn cell developed by KNUTD



Discharge curves for AAA MnO_2/Zn battery, as well as air-metal cells based on PANI and PPY catalytic electrodes (I=10 mA)

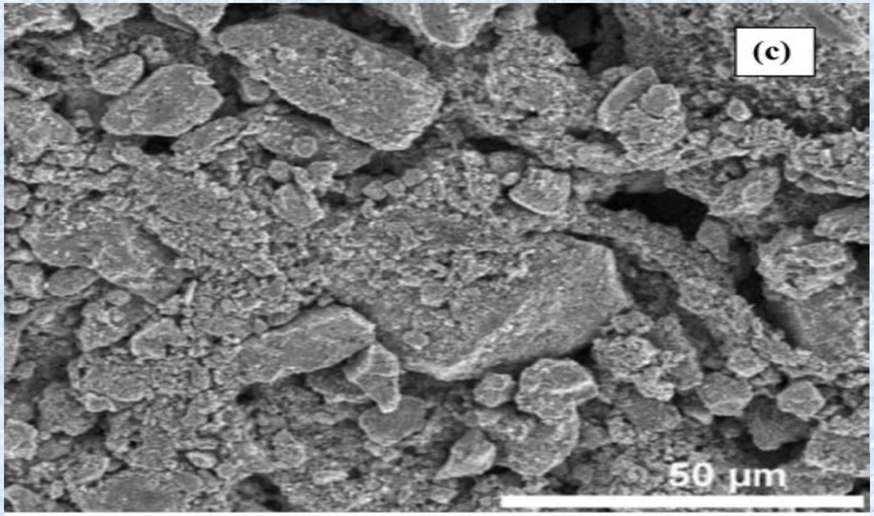


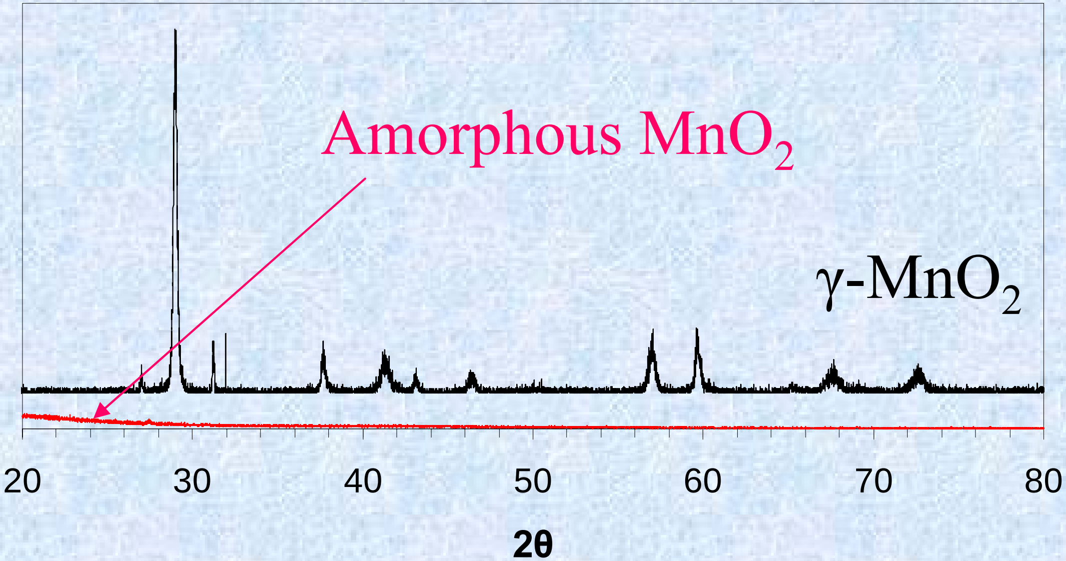
Characteristics of pilot AAA cell developed by KNUTD

Characteristics of cells	O_2|PAN| Zn	O_2|PAN| Mg	MnO_2| Zn
Discharge capacity, mA•h	420	340	380
Specific energy, W•h/kg	140	200	45
Weight of the cells, g	3	2.7	11
Dimensions, cm (H / d)	4.5 / 1.0	4.5 /1.0	4.5/1.0
Open circuit voltage, v	1.2	1.8	1.5
Discharge voltage, v (at $R_{DISCHARGE}$ = 200 Om)	1.0	1.6	1.1-1.3
Short - circuit current, A	1.0	1.2	1.4
Storage time in the serviceable condition, years	4 ... 5	<1	<2
Self - discharge, % within a month	1.5-2.0	2.0-4.0	1.0-3.0
Rechargeability, cycles	≥ 50	------------	----------

Synthesis of amorphous manganese oxide

SEM's micrographs of amorphous MnO_2

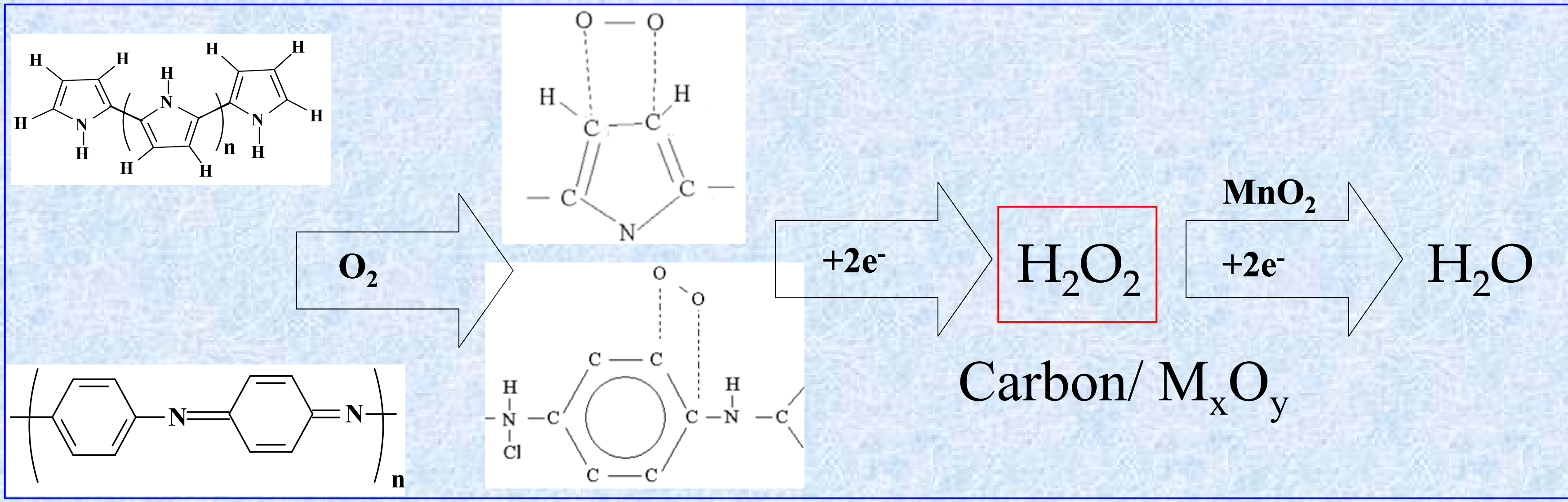




XRD of amorphous MnO_2 and γ-MnO_2

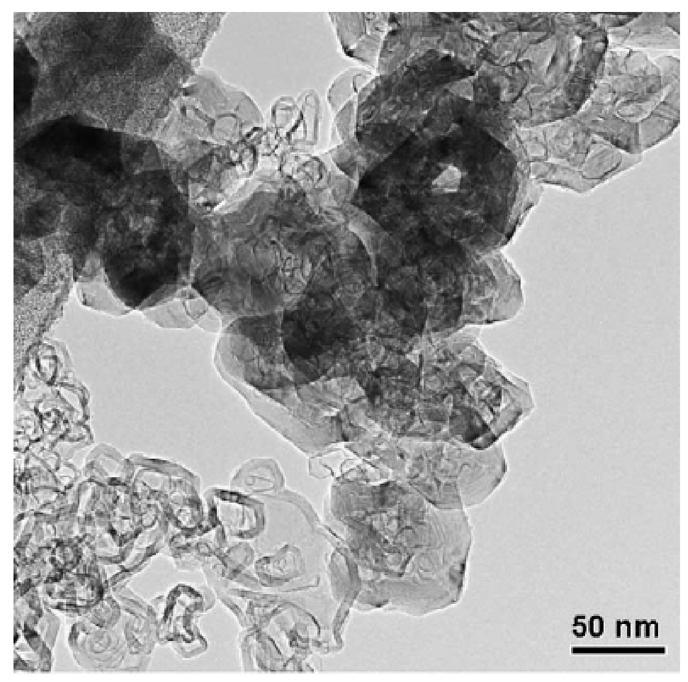
The amorphous manganese oxide was prepared by a coprecipitation method by mixing solutions contaning Mn (II) and Mn(VII)

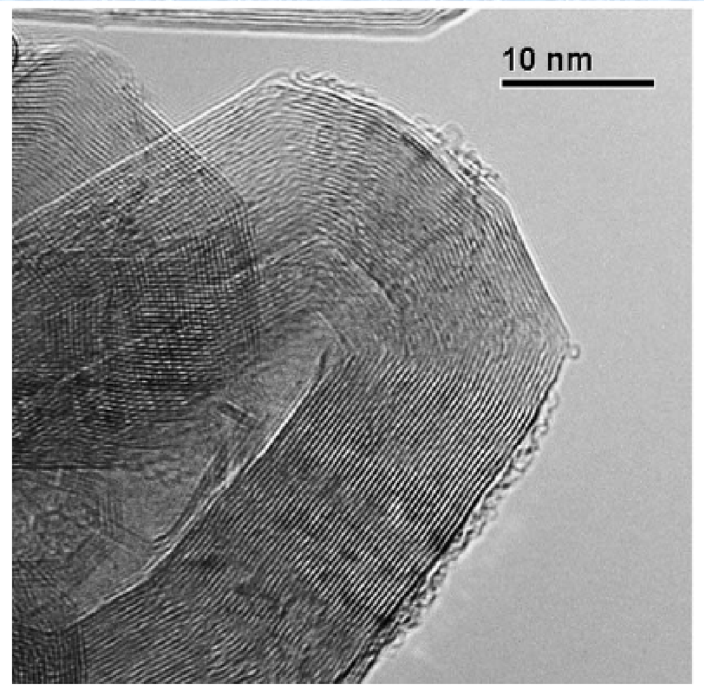
Oxygen gas-diffusion electrode based on conducting polymers and amorphous MnO_2 (AMD)



The application of composite based on CPs, as well as carbon materials modified by catalyses of H_2O_2 decomposition like MnO_2 is a very promising way to improve a catalytic activity.

Morphology of graphitized carbon black (PUREBLACK) developed by Superior Graphite Co.

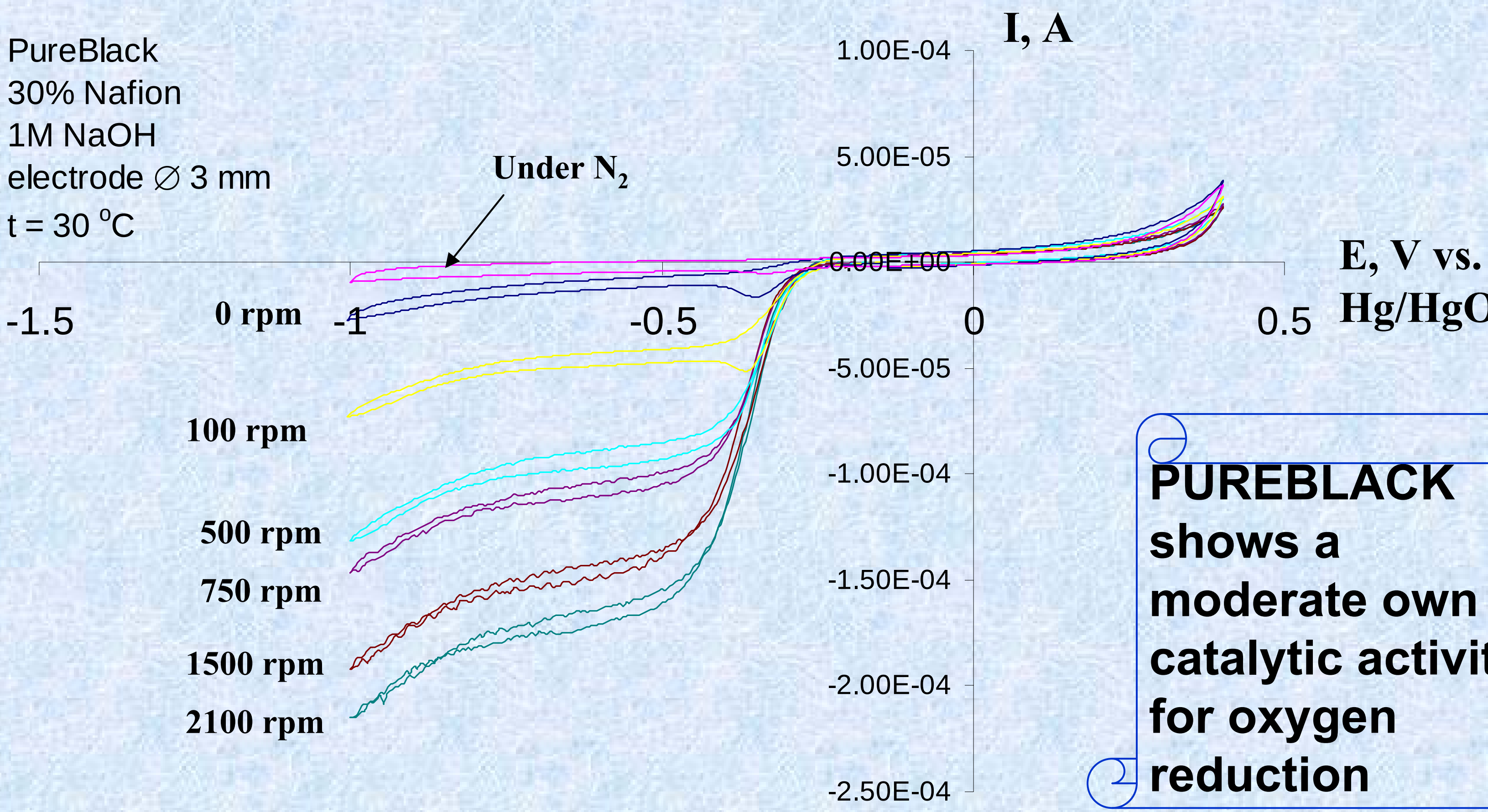




Transmission electron microscope images of graphitized carbon black, PUREBLACK®

PUREBLACK (PB) is the highest purity and low cost nano-material with BET surface about 100 m^2g^{-1}

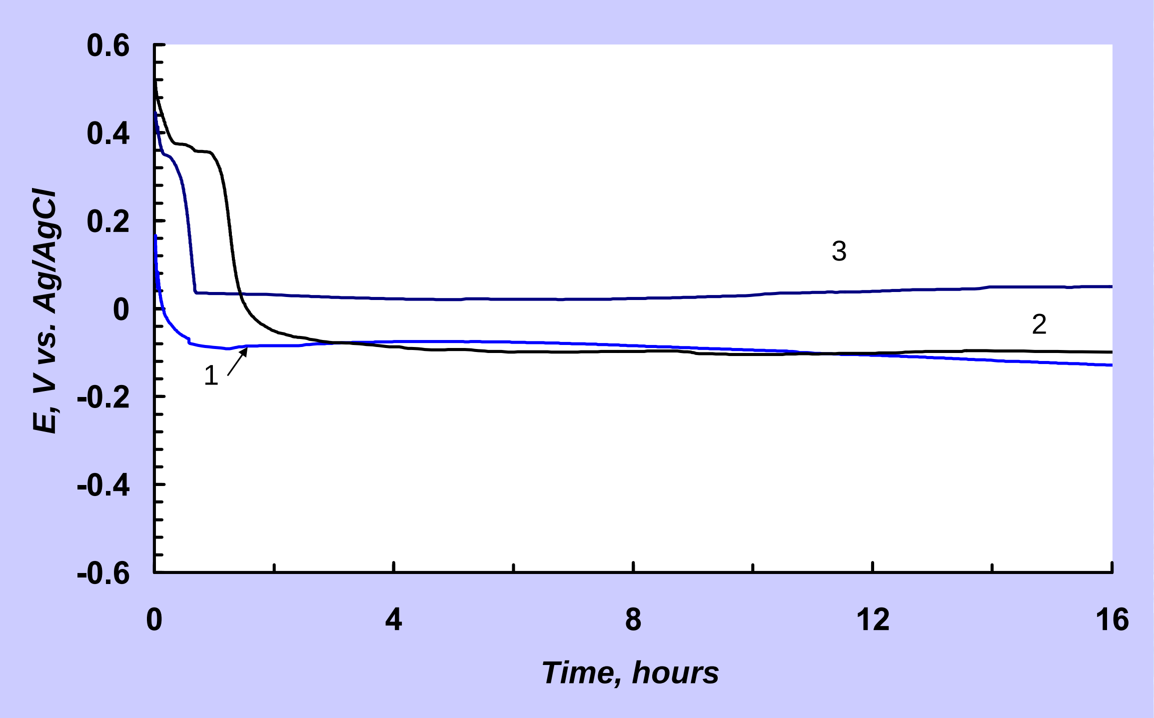
Catalytic activity of PUREBLACK towards the oxygen reduction



PUREBLACK shows a moderate own catalytic activity for oxygen reduction

CV of rotating disk electrode based on Pureblack

Galvanostatic discharge of the electrodes (S=0,5 cm²) based on PANI (1), AMD (2) and PANI/AMD/PB composite (3) in the 40% $ZnCl_2$ solution at the current density 20 mA/g.



The potential of oxygen electroreduction at the composite ***PANI/AMD/PB*** electrode is of about 150 mV higher then on other catalysts. **It is very promising composite for oxygen gas-diffusion electrode.**

Conclusion -2

1. *The catalytic activity (CA) of practically all types of conducting polymers (PANI, PPy, PTh, PMTh, etc.) towards the oxygen reduction has proved experimentally. PANI demonstrates the highest CA among the other ECPs, PEDOT does not have CA at all.*
2. *Quantum-chemical calculations of the electronic structure of the ECPs…O2 adsorption complexes gave possibility to explain the reasons and mechanisms of ECPs CA as result of shifting the electron density from the ECP surface to the chemisorbed oxygen molecules, increasing in the O-O bond length and decreasing in the bond orders.*
3. *Macro-kinetic investigations shown that ECPs CA depends strongly on oxygen content and type of conducting support. Thermo-exfoliated graphite has recommended as quite good support for realization of ECPs based porous gas-diffusion electrode.*
4. *Composites of PANI with Amorphous MnO2, graphitized carbon black (PUREBLACK) demonstrate the best CA and could be used as promised composite catalysts for oxygen gas-diffusion electrode.*