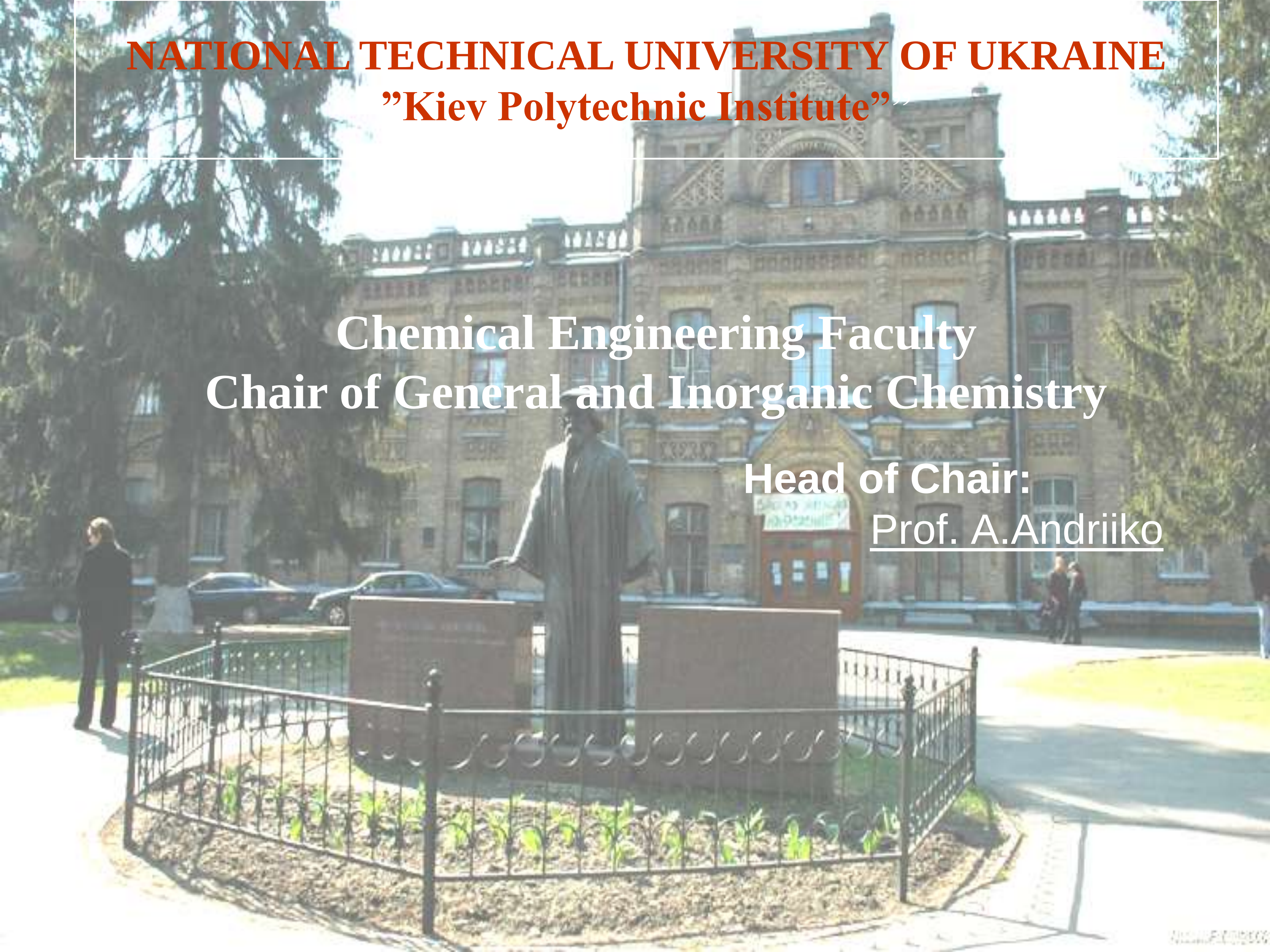


NATIONAL TECHNICAL UNIVERSITY OF UKRAINE
”Kiev Polytechnic Institute”

Chemical Engineering Faculty
Chair of General and Inorganic Chemistry

Head of Chair:

Prof. A.Andriiko

Chair of General and Inorganic Chemistry: main research directions

1. **Coordination chemistry of metal complexes with aminoalcohol ligands**. These researches were started since 1960-s by Prof.V.V.Udovenko

- *Synthesis, structural researches, applications*
- *Kinetics and mechanisms of ligand substitution reactions*
- *Equilibriums in solutions of complex compounds*

2. **Electrocatalysts based on pyrolysis products of d-metals polynuclear complexes**

- *Electrochemical reduction of oxygen (together with IGICH)*
- *Electrochemical intercalation of Li into graphite structure*

3. **Electrochemically active oxide materials for energy storage systems**

- *Complex oxides of Li-Me-O (Me=Mn,Co,Ni,Fe,Cr,…) systems with layered and spinel structures*

4. **Nanosized metal oxides for energy storage and other applications**

Nanosized cathalytic centres on the surface

1. Synthesis of the polynuclear complexes of 3d-metals with aminoalcohol ligands:

2 *fac*- $Co(Etm)_3 + Me(NO_3)_2 \rightarrow [Me(Co(Etm)_3)_2](NO_3)_2$

Generally, reaction of the tris-aminoethylates of Co(III) with metal salts are used. This is the universal and convenient method for the preparation of various polynuclear Co-Me complexes (Me = Ni, Zn, Cu, Fe etc.). The complex of Co behaves as an independent ligand in this reaction.

2. Grafting of the complex onto the surfase of a carrier (graphite or other carbon material, e.g. nanotubes) followed by pyrolysis in an inert media.

As a result, nanosized spinel structured catalytic centres are formed :

$[Ni(Co(Etm)_3)_2](NO_3)_2 \rightarrow (NiCo_2O_n)_{x}$-C(graphite) + (volatile products)↑

Thus modified, the materials demonstrate the catalytic activity with regard, at least, to 3 kind of electrochemical reactions: 1) reduction of oxygen; 2) intercalation of Li and discharge-ionization of hydrogen

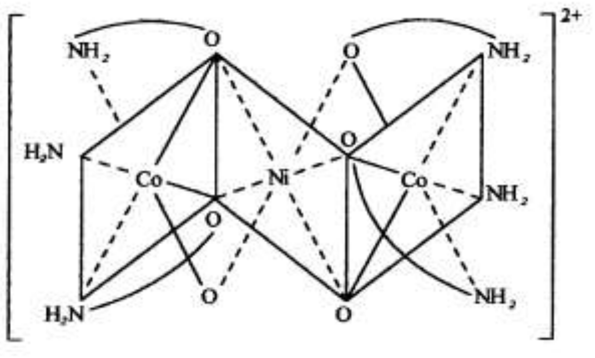
Polynuclear 3d-metal complexes with ethanolamines

1.Synthesis:

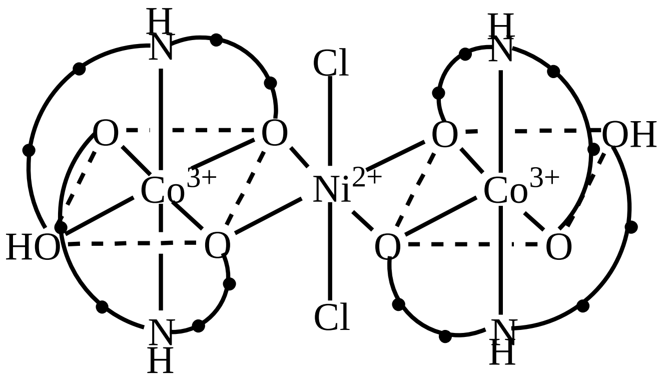
$2\ \textit{fac}\text{- }Co(Etm)_3 + Me(NO_3)_2 \rightarrow [Me(Co(Etm)_3)_2](NO_3)_2$

Generally, reaction of Co(III) trice-aminoethylate isomers with metal salts is used. It is a convenient and universal method for preparation of various polynuclear Co-M complexes (Me = Ni, Cr, Zn, Cu, Fe and others). The inner complex compound of Co(III) behaves as a separate polydentate ligand in this interesting reaction.

2. Structure:



or



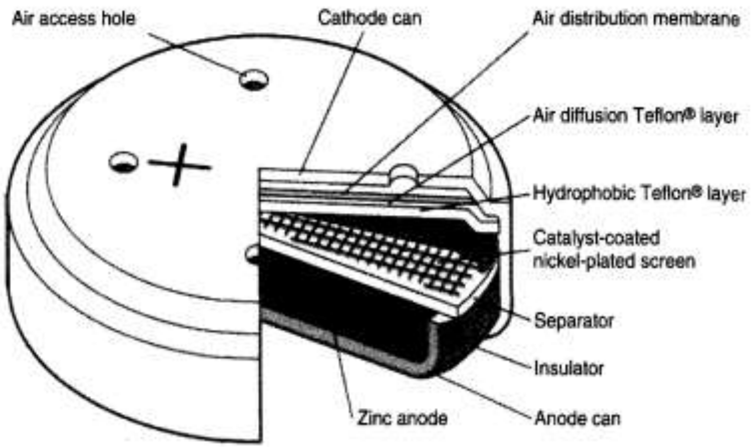
Polynuclear 3d-metal complexes with ethanolamines

Electrocatalysts based on pyrolysis products

I. Reduction of O_2.

Practical application – in metal-air electrochemical cells
(usually – cells of Zn/O_2 system)

Disk-type cell of zinc-air system



Chemistry of Zn/O_2 cell

Total reaction

$Zn + 0.5O_2 = ZnO$, $E^0 = 1,65B$

Anode (-)

$Zn + 2OH^- = Zn(OH)_2 + 2e^-$

$Zn(OH)_2 \rightarrow ZnO + H_2O$

Cathode (+)

$O_2 + 2H_2O + 4e^- = 4OH^-$

stages:

1) $O_2 + H_2O + 2e^- \rightarrow OOH^- + OH^-$
2) $2OOH^- \rightarrow O_2 + 2OH^-$ (повільна)

The cathode always incorporates a **catalyst** for peroxide decomposition reaction, which enhances the whole process.

The metals (Pt, Ag) transition metal oxides, rare earth metal oxides with spinel and perovskite structures, as well as macrocycle metal complexes (phtalocyanine, porphirine) are used most often for this purpose

Electrocatalysts for electrochemical reduction of oxygen

- The data are already available on:
- The nature of ligand
- The nature of metals
- Pyrolysis temperature

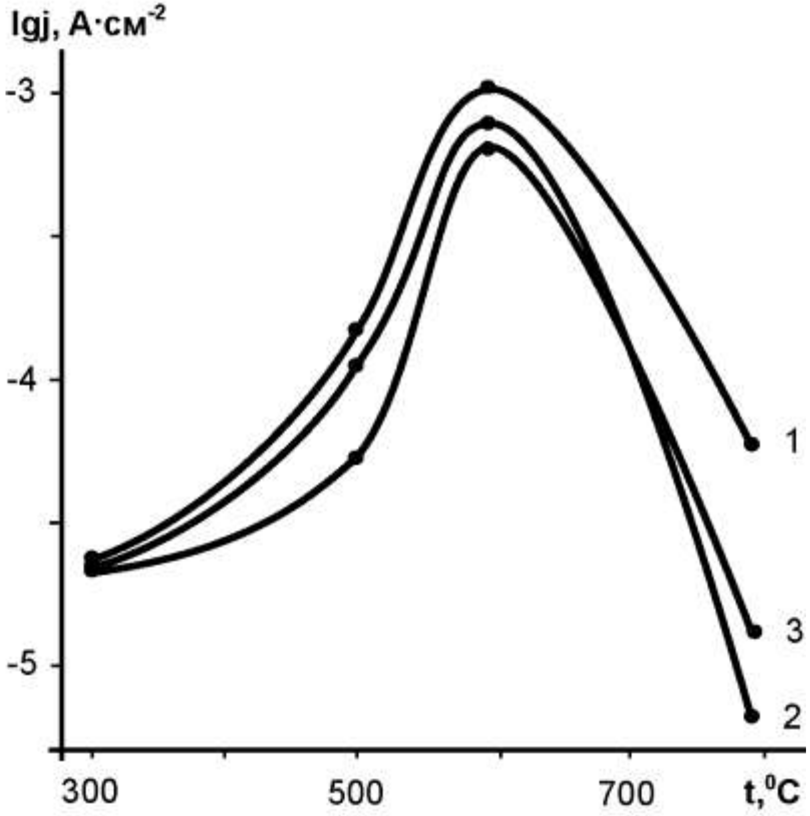
The Figure shows the dependence of catalytic effect on the nature of ligand and pyrolysis temperature for one type of the studied complexes:

Me[CoEnDetmOH]$(NO_3)_2$

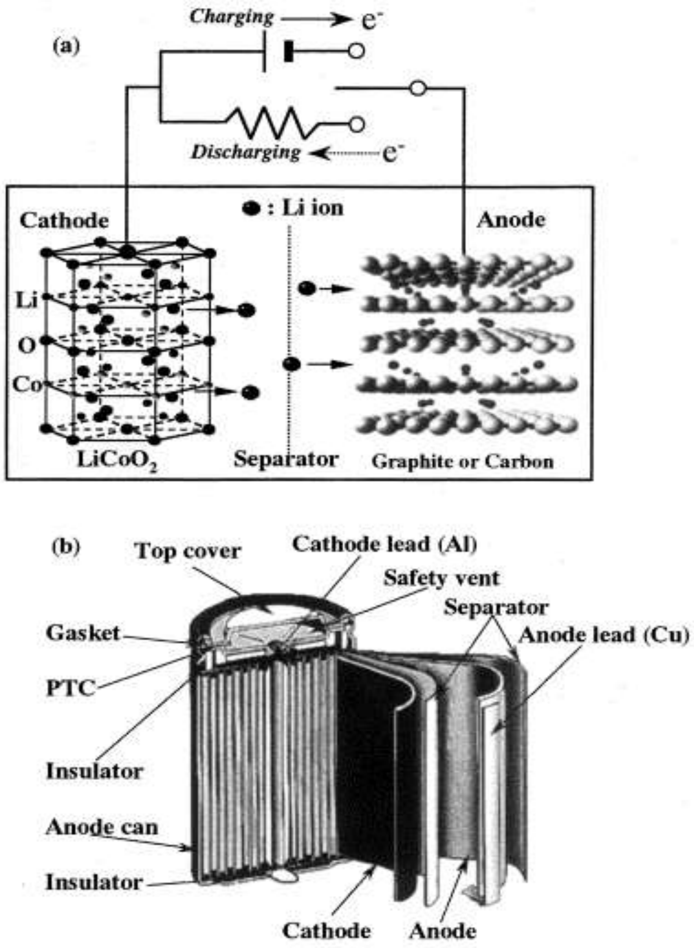
Co – Ni – ***1***,

Co – Zn - ***2***;

Co – Cu - ***3***



Lithium-ion battery. Operation principles and scheme of cylinder-type cell



Electrode processes:

Negative

$xLi^+ + xC + e^- \Leftrightarrow LiC_x\ (x \geq 6)$

Positive

$LiCoO_2 \Leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$

Simplified overall reaction

$2LiCoO_2 + 6C \Leftrightarrow 2Li_{0.5}CoO_2 + LiC_6$

(Discharge →; charge ←)

Negative Electrode

Common material – **graphite**

Shortcomings:

- theoretical specific capacity 375 mAh/g, practically – not exceeds 270-300 mAh/g
- low power properties – the capacity decreases very quickly as current load increases
- flammability and combustibility in charged state

Negative electrode. Modification of graphite by pyrolysis products of the complexes

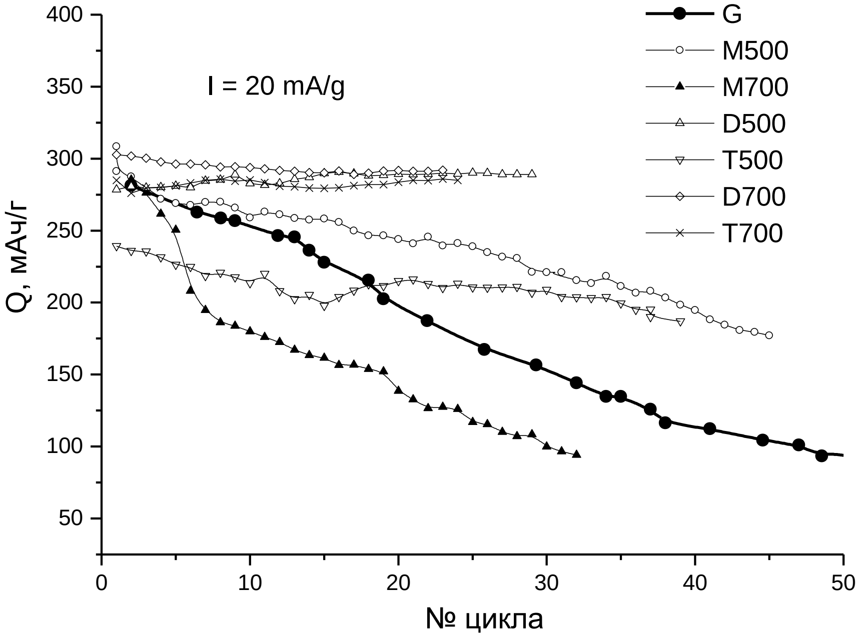
- •Catalytic effect of the pyrolysis products on the reaction of Li intercalation into graphite was first discovered by us in 2003. Since then, a number of investigations were carried out for trinuclear complex 2Co-Ni.
- •The folliving factors were studied:

-Nature of the ligands

-Type of graphite

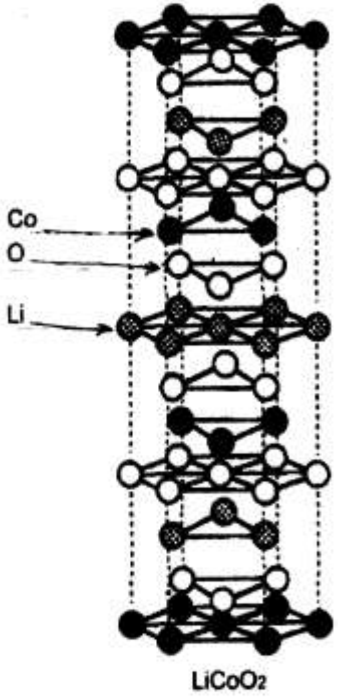
-Temperature of pyrolysis

- Current load



The figure shows changes in capacity for initial and modified graphites in course of durable cycling. The letters in the samples marks denote ligand, numbers – pyrolysis temperature, ^{o}C.

Positive electrode

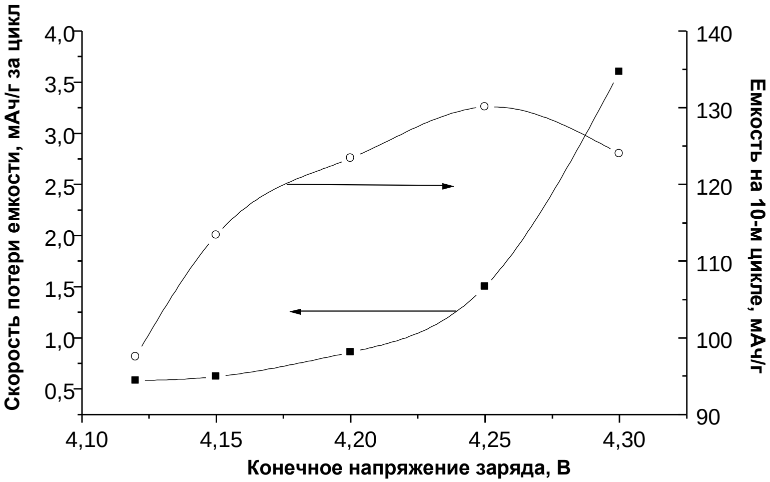


Standard material – **lithium cobaltate** with α-NaFeO$_2$ type of structure

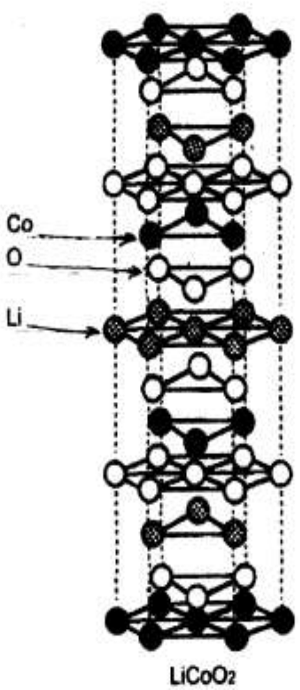
Theoretical capacity 137 mAh/g, which corresponds to the reaction $\mathbf{LiCoO_2 \Leftrightarrow Li_{0.5}CoO_2 + 0.5Li^+ + 0.5e^-}$

Drawbacks:

- High cost
- Toxicity of Co compounds
- Sensitivity to incidental overcharge



$LiNiO_2$ as an alternative to $LiCoO_2$



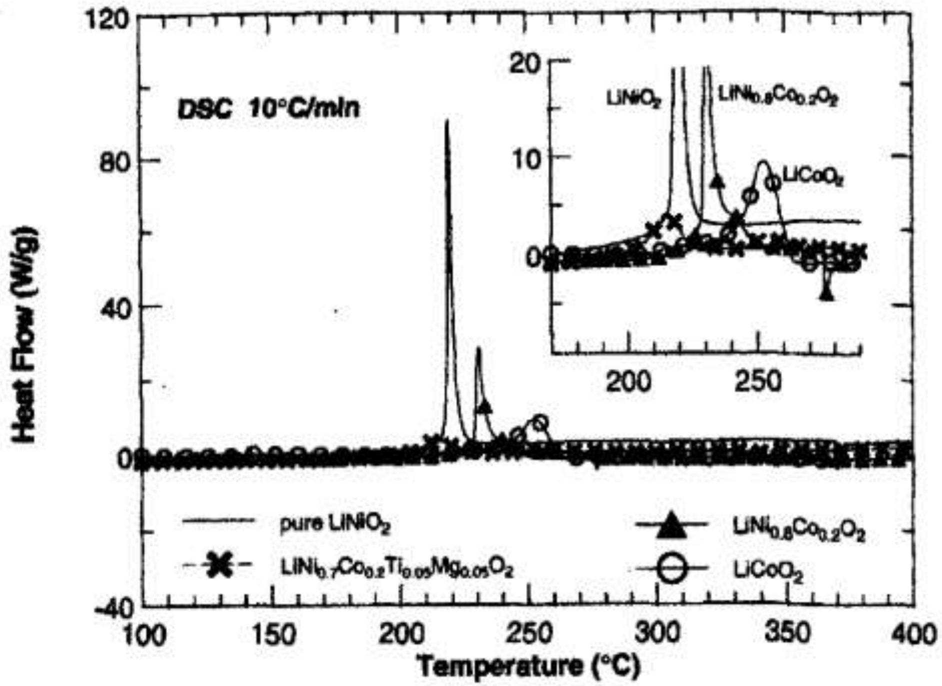
Structure is the same. Theoretical capacity is even higher because the structure withstands higher withdrawal of lithium

Shortcomings:

- Very complicated synthesis, with properties of the product being poorely reproducible
- Structure is less stable, especially on heating
- Higher rate of capacity loss at cycling as a result of relative instability of the structure

Thermal instability of α-$NaFeO_2$-type compounds

(espacially $LiNiO_2$)

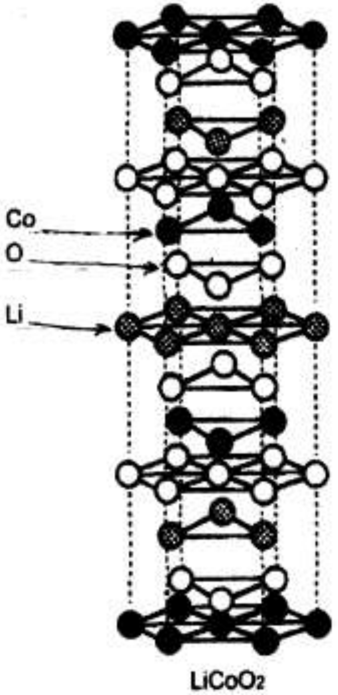


DSC of charged materials with layered structure

Ways for improvement of positive electrode materials

1. Improvement of $LiCoO_2$ structure by partial replacement of Co atoms with other metals
2. Use of the compounds with lithium-manganese spinel $LiMn_2O_4$ basic structure
3. Novel materials of positive electrode

Improvement of $LiCoO_2$ structure



$LiCo_{1-x}Fe_xO_2$ (M. Holzapfel et al, 2001)

$LiCo_{0.5}M_{0.5}O_2$ (M=Ni, Mg, Mn, Zn);

$LiM_{1-y}M_y'O_2$ (M=Ni, Co and M'=Mg, Al, B) (C. Julien et al, 2000)

$Li_{1-z}Ni_{1+z}F_yO_{2-y}$; $Li_{1-z}Mg_xNi_{(1-x)(1+z)}O_2$ (AR Naghash, JY Lee , 2001)

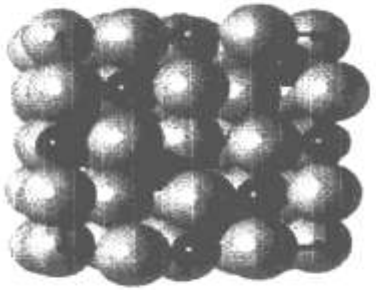
$LiGa_xMg_yN_{1-x-y}O_2$ (A Yu, GVS Rao, BVR Chowdari, 2000)

$Li_1\ Ni_{1-y}\ M_y\ N_x\ O_p$, wherein **M** is a transition metal selected from **Ti, V, Cr, Mn, Fe, Co,** and **Al,** and **N** is a group II element selected from **Mg, Ca, Sr, Ba**, and **Zn**. *Pat USA 6017654, Jan. 25, 2000*

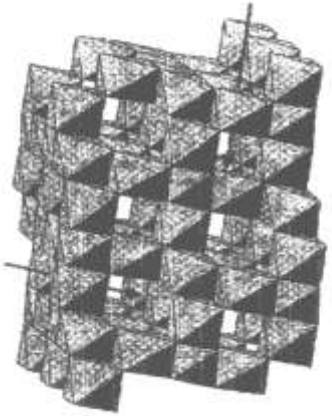
Main approach – consists in replacement of Co atoms with other metal. A few works are known, where partial replacement of oxygen atoms with F was used.

We have started a cycle of systematic studies for the possibility of this approach (future PhD thesis of A.Shpak).

Structures of $LiMn_2O_4$ spinel



$LiMn_2O_4$



λ-MnO_2

$LiMn_2O_4 \Leftrightarrow Li_\delta Mn_2O_4$ (λ-MnO_2) + $(1-\delta)Li^+$ + $(1-\delta)e^-$

Capacity: theory 148 mAh/g; practically 120, inexpensive, non-toxic

Instability, sensitivity to accidental overdischarge

$Li_{1+x}Mn_{2-x}O_4$ (110 mAh/g, stable)
$LiAl_xMn_{2-x}O_4$ (120 mAh/g, stable)
$LiMn_{1.8}Mg_{0.2}O_4$ (H Aikiyo et al, 2001)
$LiCo_xMn_{2-x}O_4$ (B W Lee, 2002)
$LiNi_{0.5}Mn_{1.5}O_4$ (X Wu and S B Kim, 2002)
$LiSe_{0.1}Mn_{1.9}O_4$ (C. S. Yoon et al, 2002)
$Li_{1.02}Mg_{0.1}Mn_{1.9}O_{3.99}S_{0.01}$ (S H Park et al, 2001)
$LiMn_{2-x}V_xO_4$ (KR Murali et al, 2000)
$Li[M_xMn_{2-x}]O_4$ (**M = Co, Al** and **Ti**) (SH Yang, RL Middaugh, 2001)
$Li(Mn_{2-x}Li_{x/4}Co_{3x/4})O_4$ (YS Hong et al, 2001)

Main approach – consists in replacement of Mn atoms with other metal. A few works are known, where partial replacement of oxygen atoms with F was used.

We have started a cycle of systematic studies for the possibility of this approach

Lithium-ion battery. Safety problems.

Behaviour of standard battery at accidental depressurization

What does this mean for my product?

Non-carbon materials can solve the safety problems of Li-ion batteries

- **SnO** and **SnO2 -**based materials (STALION trademark), Fujifilm Celltech

(*Can Pat Appl*, 1994 2,1135053; *Eur Pat Appl*, 1995,651450 A1 950503.)

1) $SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O$, 2) $xLi^+ + Sn + xe^- \Leftrightarrow Li_xSn$, ($x_{max}$ =4,4)

(I-st cycle capacity is about 1400 mAh/g; reversible capacity 600-700 mAh/g)

Particle size is very essential – the smaller the particles, the better.

- ***Nanosize metal oxides***: $MeO_x + 2xLi^+ + 2xe^- \Leftrightarrow Me + xLi_2O$

  CoO (300 mAh/g; G. X. Wang et al, 2002; 700 mAh/g; P Poizot et al, 2000)

  SnS_2 (250 mAh/g; T.Brousse et al, 2002)

  TiO_2 (285 mAh/g; A. Kuhn et al, 2001)

  $LiMVO_4$, M=Co, Ni, Cd, Zn (600 mAh/g; R.K.B. Gover et al, 1999)

  Zn_2SnO_4 (500 mAh/g; F. Belliard et al, 2001)

Synthesis of the oxide nanopowders by oxidation of metals or metal compounds in molten nitrate media

General reaction of the metal oxidation:

$$\mathbf{2Me + zNO_3^- + (2n\text{-}z)O^{2-} = 2MeO_n^{z-2n} + zNO_2^-}$$

Conclusion: *The composition of the product depends on the basicity of the melt*

According to the Lux-Flood theory, the basicity of such melts is determined by the activity of O^{2-} ions:

$$\mathbf{Me^{z+}\ (acid) + nO^{2-} \Leftrightarrow MeO_n^{z-2n}\ (base)}$$

In the “neutral” nitrate melt, the oxygen ions result both from the reduction of nitrate

$NO_3^- + 2e^- = NO_2^- + O^{2-}$; $NO_3^- + e^- = NO_2 + O^{2-}$,

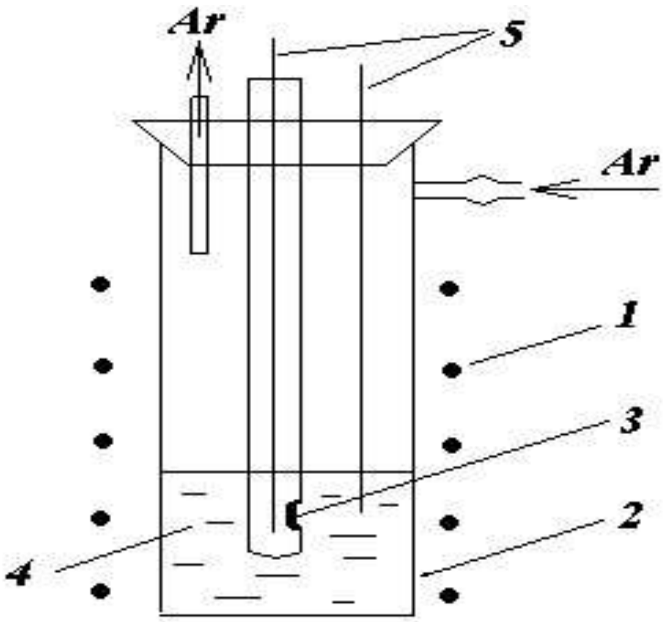
and its dissociation $NO_3^- \Leftrightarrow NO_2^+ + O^{2-}$

In order to obtain the desired composition of the product, the basicity of the media should be adjusted by means of “acid” (bounding the ions O^{2-}) or “basic” (forming the ions O^{2-}) additives.

Electrochemical cell

Pt | KNO_3 – $NaNO_3$ || KNO_3 – $NaNO_3$ + Ti + additive | Pt

for the experimental measurement of the basicity of the melt



$$E = \frac{RT}{2F}\ln\frac{a_{O^{2-}}(st)}{a_{O^{2-}}}$$

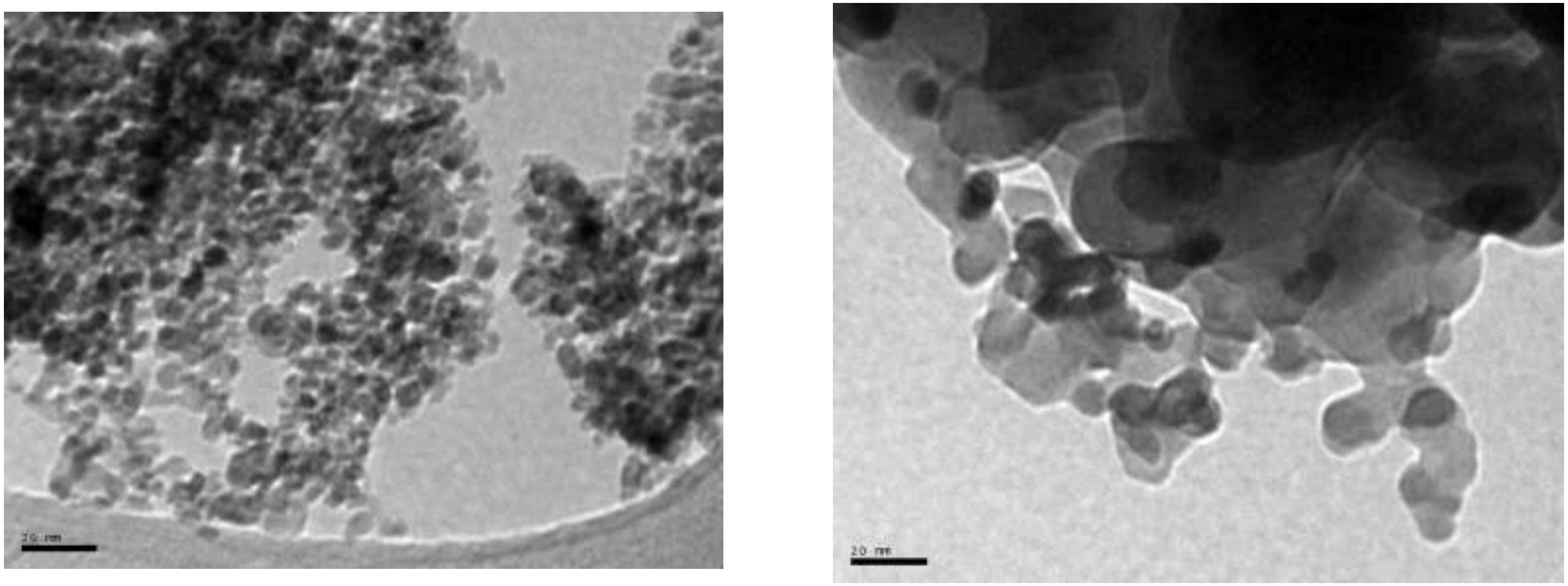
“Neutral” melt: E=0
“Acid”: E>0
“Basic”: E<0

The notations on the figurei:

1 – electric furnace; 2 – alumina crucible; 3 – alumina vessel with diphragm, containing the investigated melt; 4 – equimolar KNO_3-$NaNO_3$ melt; 5 – Pt electrodes.

Nanosized SnO_2

Synthesis method – oxidation of Sn(II) compounds in the “neutral” nitrate melt : $SnCl_2 + 2MeNO_3 = SnO_2 + NO_2 + 2MeCl$

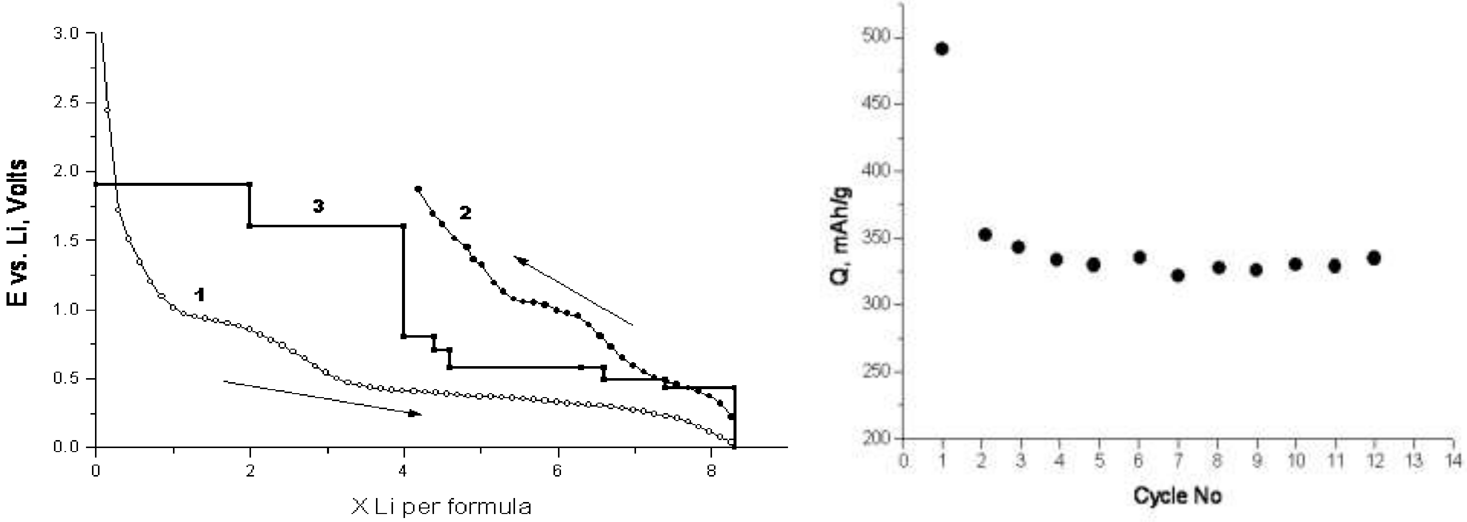


TEM image of the “fresh” product (left) and after 2 years storage (right).
Nanosized crystals tend to grow spontaneously during long time storage!

Nanosizes SnO_2: electrochemical activity

The mechanism of the electrochemical reduction

$$5SnO_2 + 42Li \rightarrow 10Li_2O + 5Sn + 22Li \Leftrightarrow Li_{22}Sn_5 + 10Li_2O$$



The first charge and discharge curves (left). The staircase line 3 corresponds to the thermodynamically calculated data for the stepwise reduction. The reversible capacity vs. the cycle No is shown in the left figure.

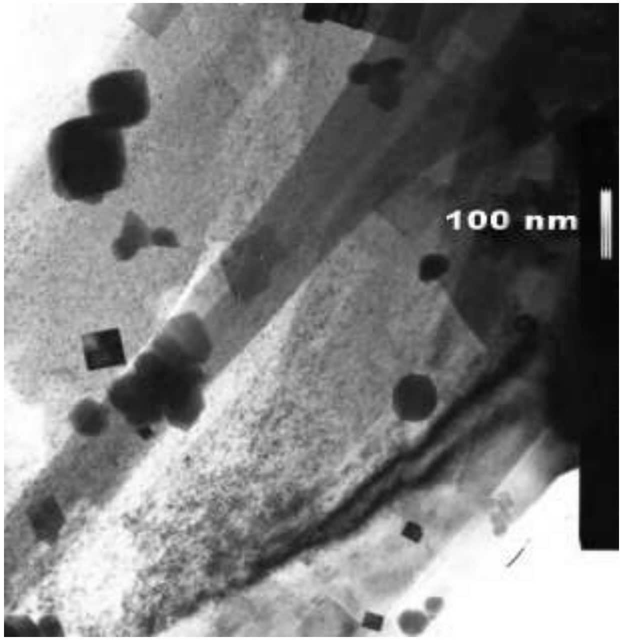
Potassium tantalate $KTaO_3$

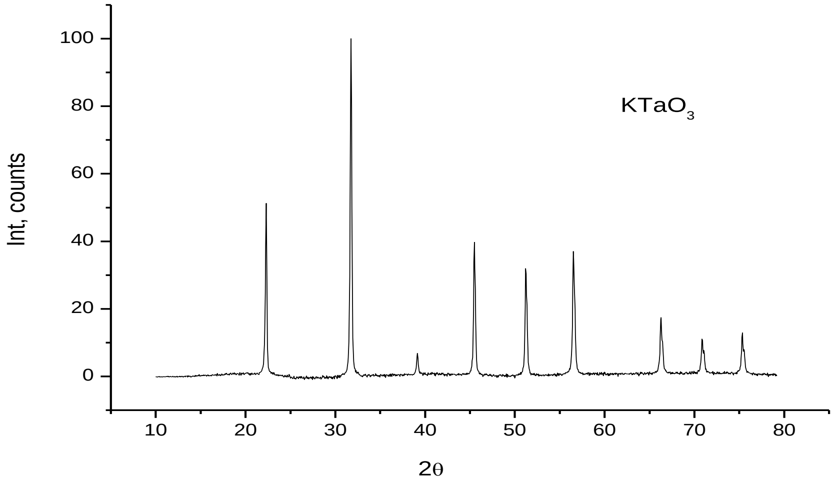
Perovskite structured, ferroelectric, ε ≈ 300-350.

Synthesis:

Oxidation of Ta powder in a “basic” melt (addition of KOH):

$$2KOH + 2Ta + 5KNO_3 \rightarrow 2KTaO_3 + 5KNO_2 + H_2O$$



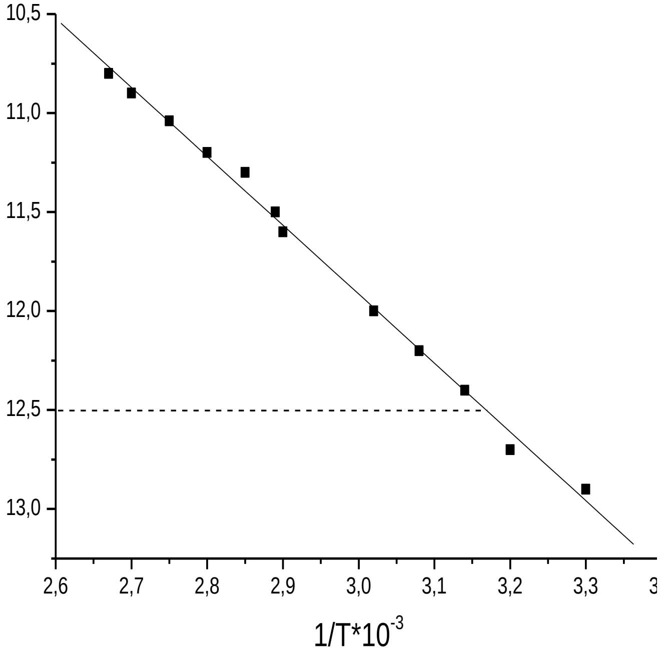


Crystal sizes ~ 80 nm

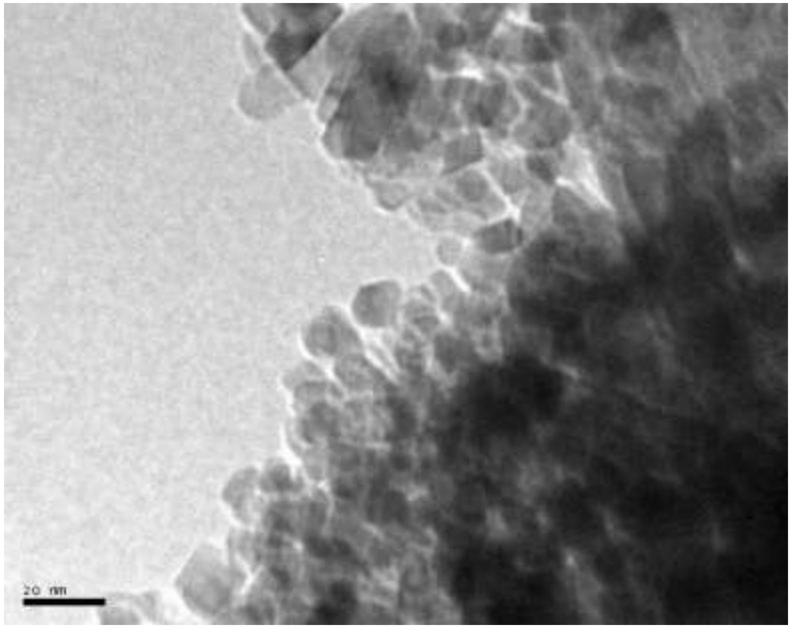
Potassium tantalate $KTaO_3$: properties

Dielectric permeability of the tablets is about 300-360.

Unexpectedly, the samples appeared to possess rather significant semiconductor conductivity. It is equal to 10^{-5} Sm/cm at room temperature and increases exponentially as the temperature inctease. Such behaviour is not common for the large crystal samples.

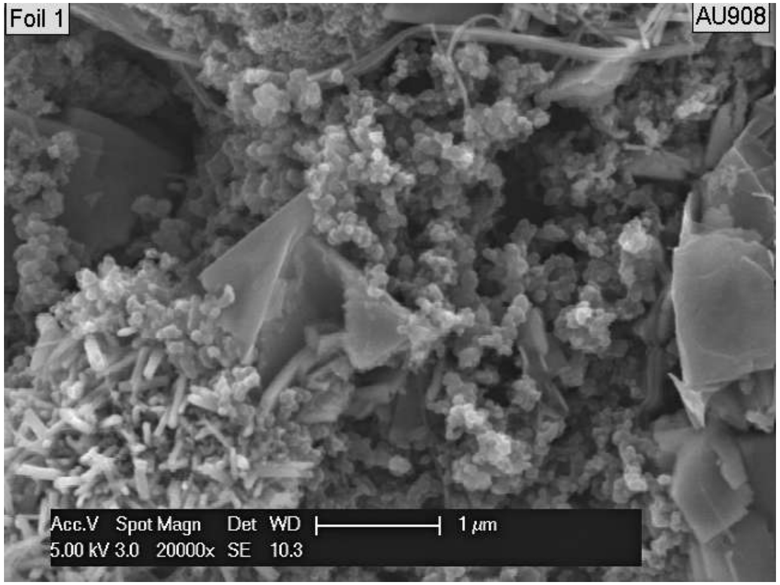


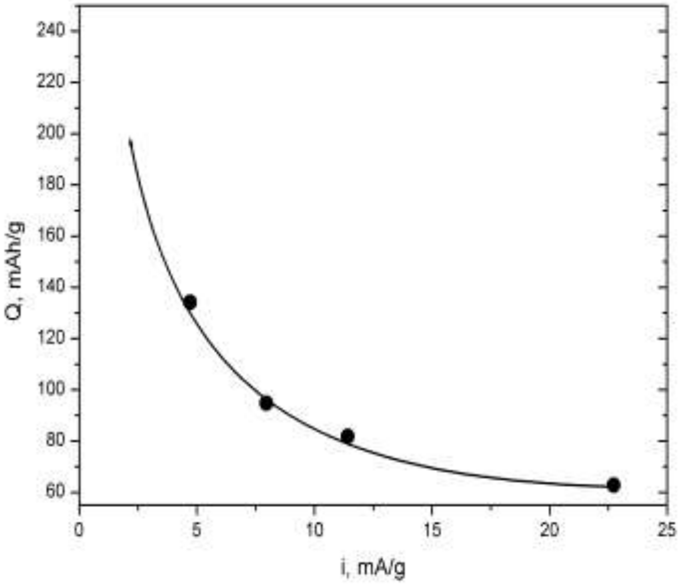
Nanosized titanium oxides



Synthesis: oxidation of the preliminary activated Ti metal powder in the nitrate melt. Depending on the basicity of the melt, common nanocrystals (left) or nanowires (right) are formed.

Problem of preparation of the electrode active mass





<u>Left</u>: The SEM image of the electrode active mass on the copper foil. The particles of the standard conductive additive (graphite powder) are much larger then the nanocrystals of TiO_2.

<u>Right</u>: As a result, the theoretical capacity could be attained at very low currents

New Concept of Safe Li-ion Battery: Carbon-free and Cobalt-free Cell

- *Negative electrode – one of the nanosized oxides*. Graphite or other carbonaceous materials are totally excluded
- *Positive electrode – lithiated oxide without toxic Co compounds*
- *Cell's reaction*, for example

  TiO_2 (nanosized) + $LiMeO_2 \Leftrightarrow Li_xTiO_2 + Li_{1-x}MeO_2$

- ***Problems***
- – irreversible loss of capacity at first charge of negative electrode material. It exists for traditional graphite also, but is much higher for the oxide materials (graphite ~ 15%, SnO_2 ~ 47%).
- – bad electric contact of the nanoparticles with the current leads

- *How to overcome?*

  (development of "overstoichiometric" spinel oxides could be a solution)

Carbon-free Lithium Battery – the Problem

- <u>**What could be a source of Li for compensation of the irreversible loss?**</u>

1) *<u>Common approach</u>* is to increase the amount of positive electrode material. This way is not good – the specific energy and capacity of the battery fall down sharply.

2) *<u>We propose</u>* novel material for positive electrode – “overstoichiometric” spinel $Li_{1+b}[Me_nMn_{2-n}]O_4$ with increased content of lithium.

The excessive Li removes irreversibly at first charge of the cell, which compensates the irreversible loss of the negative electrode:

$Li_{1+b}[Me_nMn_{2-n}]O_4 \rightarrow Li[Me_nMn_{2-n}]O_4 + bLi^+ + be^-$,

and then works reversibly: $Li[Me_nMn_{2-n}]O_4 \Leftrightarrow [Me_nMn_{2-n}]O_4 + Li^+ + e^-$

One of such oxides, $Li_{4/3}[Mn_{4/3}Cr_{2/3}]O_4$, was already obtained and showed fairly good results. Its disadvantage – use of toxic Cr(VI) compounds in the synthesis. That is why the works are under way, which aimed at the replacement of Chromium with other metal (Fe is considered as promising substitute)

Thank you for your attention