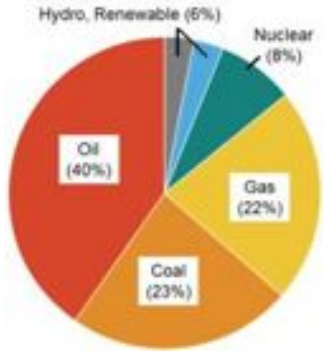
Основные тематики лаборатории материалов для электрохимических процессов

Center for Electrochemical Energy

Oil and Gas consumption degrades the environment and exhausts a critical RF resource.



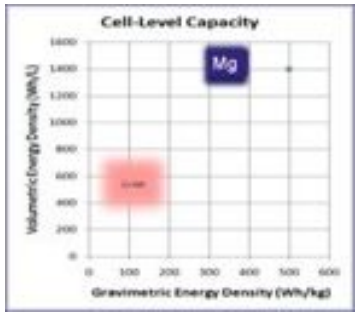
World Energy Consumption

Electrochemical energy storage provides efficient use of fossil fuels and commercial opportunities.

- Grid-level power shaping and time shifting
- Energy buffering for intermittent alternative energy sources
- Transportation and mobile devices

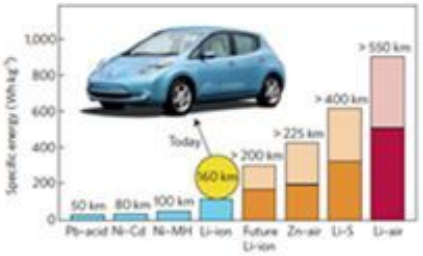
Current electrochemical energy storage technology can not meet these needs, but there are known solutions.

Advanced Li and polyvalent ion batteries



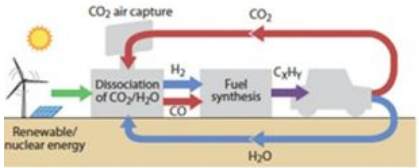
Mg^{+2} vs. Li^{+1}: 4-fold increase in capacity and density.

Rechargeable metal-air batteries



Li-ion vs. Li-air: 3-fold increase.

Fuel and Electrolysis Cells



Efficiency improvements for stationary and mobile applications.

Aqueous flow batteries

Suspension-based approaches Li-ion; with low cost, long life, safety, flexibility.

Approach

Advanced lithium ion and multivalent ion batteries

Research:

- New Li cathode materials with higher capacities or lower cost
- New cathode materials for polyvalent ions (e.g. Mg^{2+})
- Low cost organic cathode materials

Approach:

- Computational materials design
- New synthesis routes

Rechargeable metal-air batteries

Research:

- Fundamental studies oxygen reduction and evolution
- Design and synthesis of nanostructured electrodes
- Electrolyte and membrane development

Approach:

- Computational modeling
- Materials synthesis
- In-situ studies

Fuel and Electrolysis Cells

Research:

- SOFC/SOEC electrolyte materials with improved conductivity and catalytic activity
- PEMFC/PEMEC electrolyte membranes with improved conductivity/mechanical stability

Approach:

- Computational simulation and materials design
- Nanostructured electrodes, membranes and surfaces
- New synthesis routes

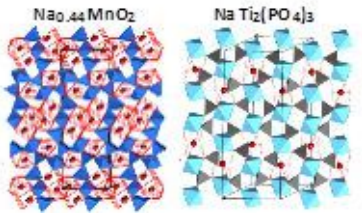
Suspension-based aqueous flow batteries

Research:

- Development of Na intercalation electrode materials
- Design and synthesis of micro/nanoporous membranes
- Device design

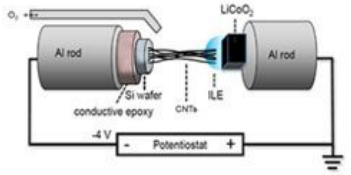
Approach:

- Computational electrochemical and hydrodynamic modeling
- Electrode and membrane materials design and synthesis



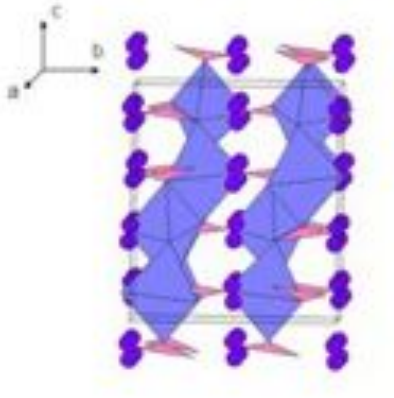
Cross-cutting themes:

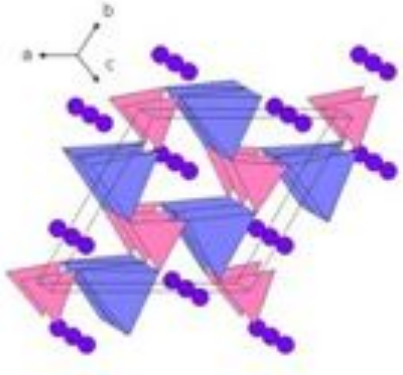
- Computational: simulation, materials and device design
- Advances in materials synthesis: molecular, nano, micro
- Advances in characterization: in-situ atomic and molecular processes
- Prototyping

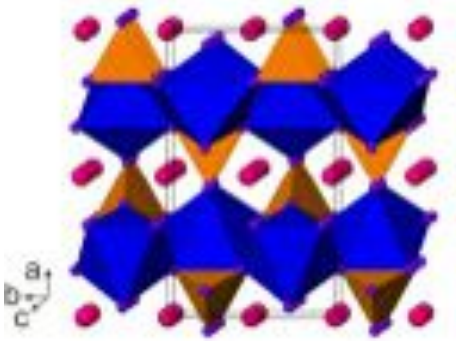


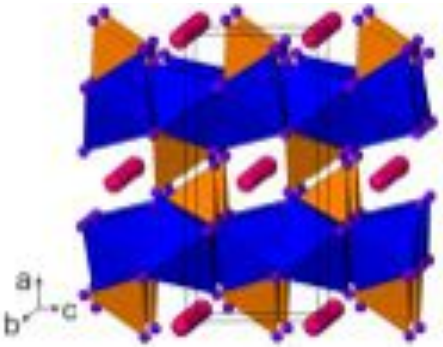
Systems level analyses

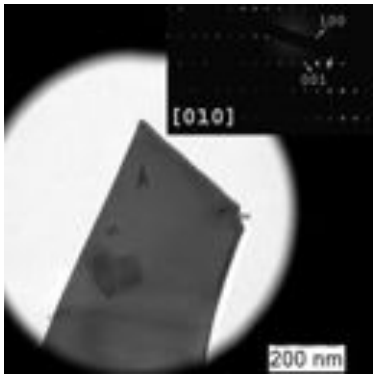
Milestones	Description	People involved
Synthesis and characterization of electrode materials	Hydrothermal and “soft chemistry” synthesis of $LiMPO_4$ and $LIMBO_3$ (M = Fe, Mn, Co). Phase analysis, electron microscopy, electrochemical measurements.	*Staff* : Dr. O.A.Drozhzhin Dr. E.V. Stenina Dr. L.N. Sviridova *Students* : V. Sumanov I. Tereschenko

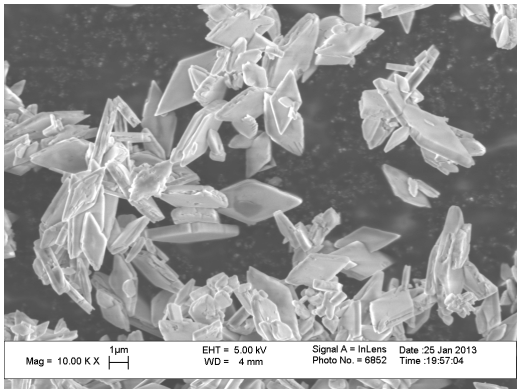


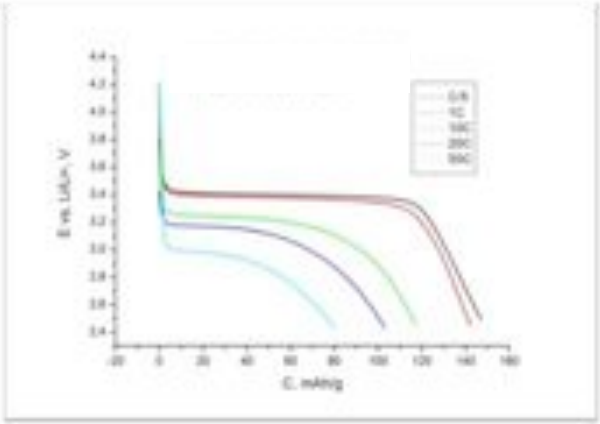




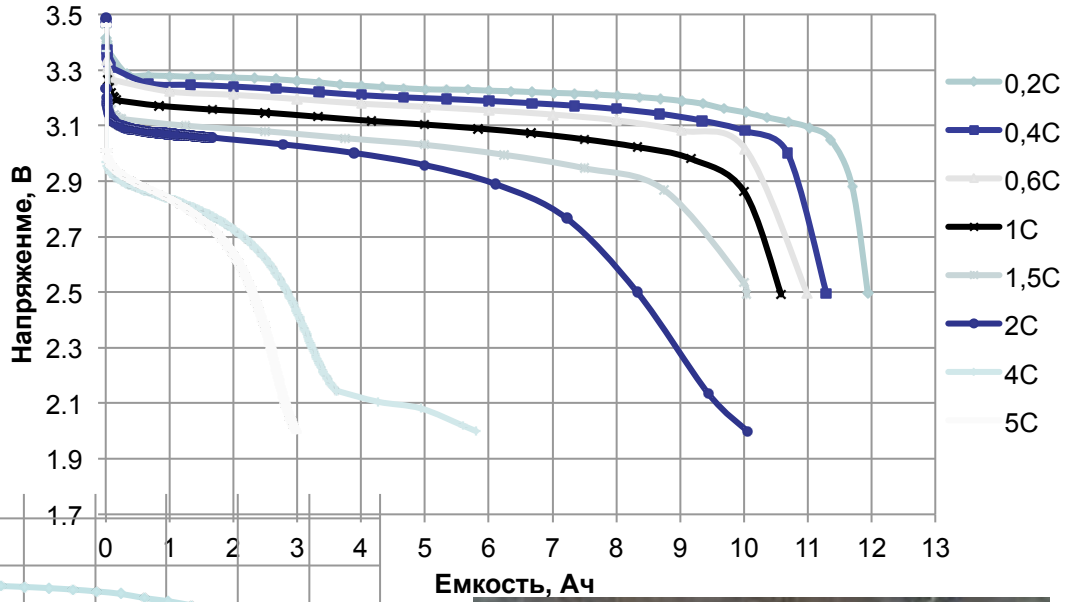


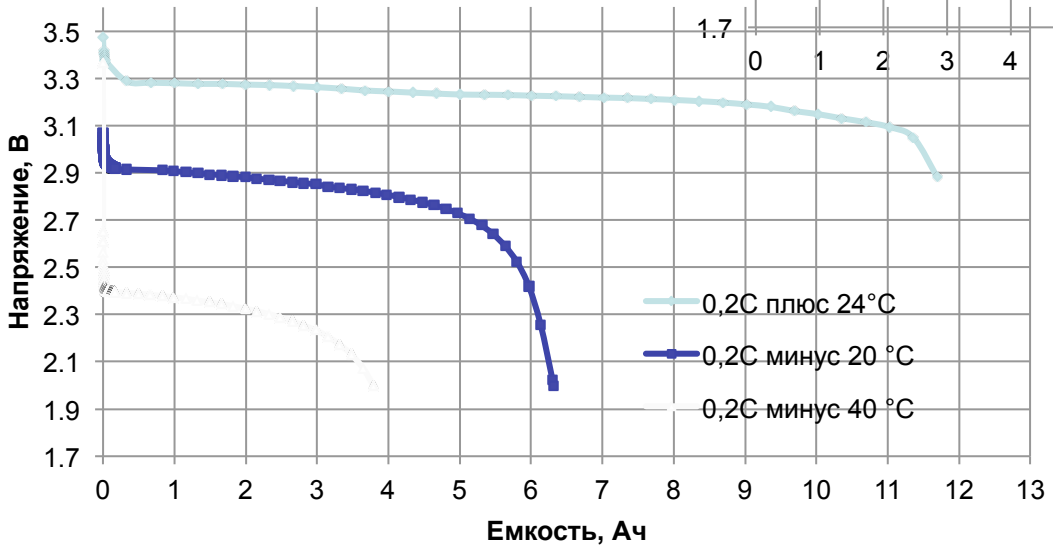




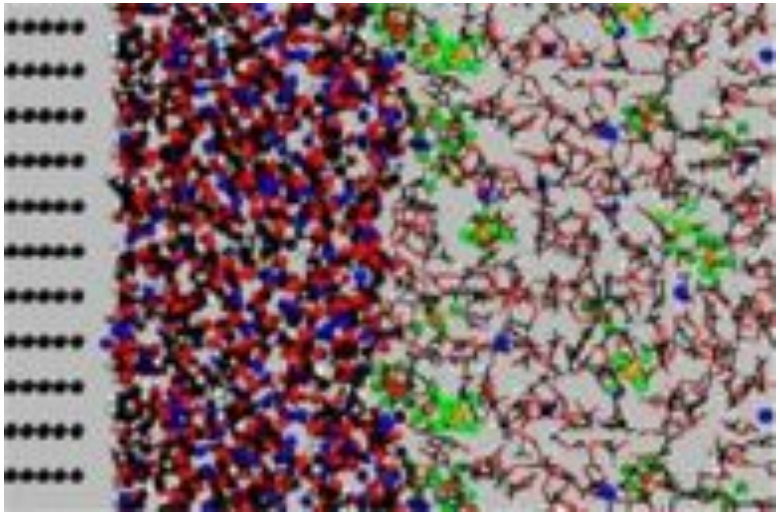


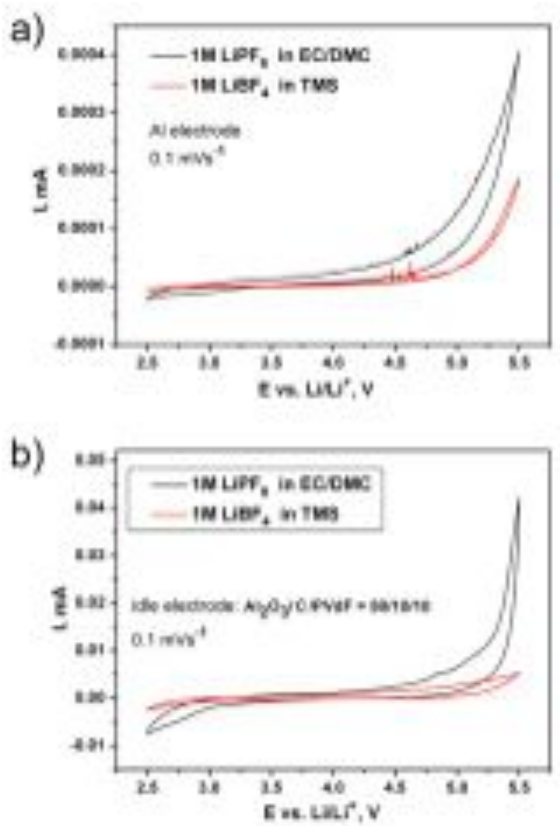
Сотрудничество:
ООО «Минерал» и НИИЭИ (Электроугли)



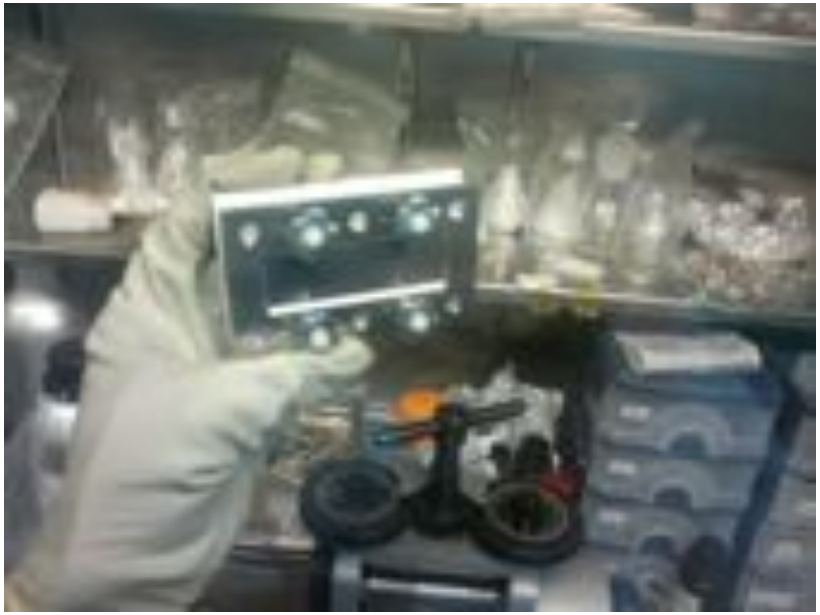


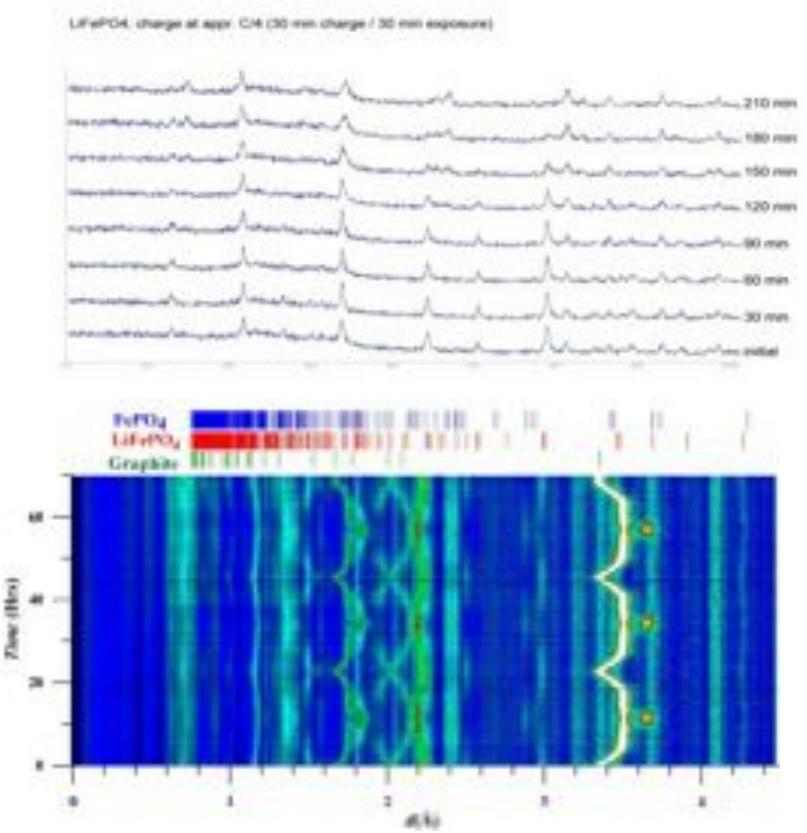
Milestones	Description	People involved
Testing of compatibility with selected electrolytes	Stability study of “high-voltage” electrolytes and ionic liquids at high potentials. Spectroscopic study and atomic modeling of solid/electrolyte interface	*Staff* : Dr. O.A. Drozhzhin **Dr. V.A. Nikitina**



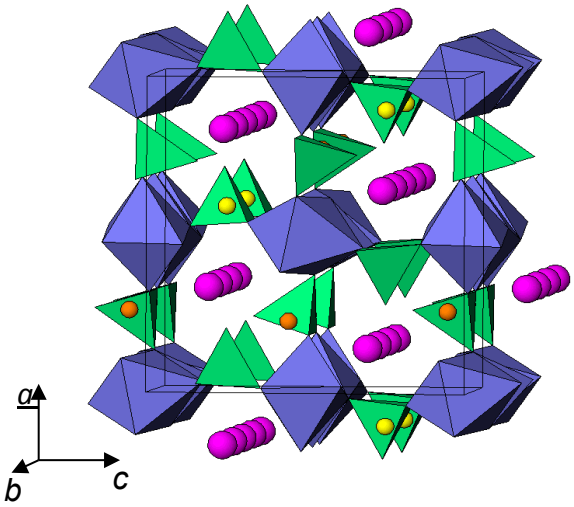


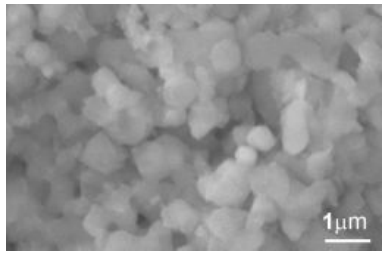
Milestones	Description	People involved
In situ X-ray, synchrotron, neutron diffraction and Moessbauer spectroscopy	Development and testing of experimental cells for *in situ* X-ray, synchrotron, neutron diffraction and Moessbauer spectroscopy. Detailed structure characterization of cathode materials stated above.	*Staff* : Dr. O.A. Drozhzhin Dr. S.M. Kazakov *In collaboration with* : Dr. I.A. Bobrikov Dr. I.A. Presnyakov Dr. B.P. Tolochko, Zubavichus

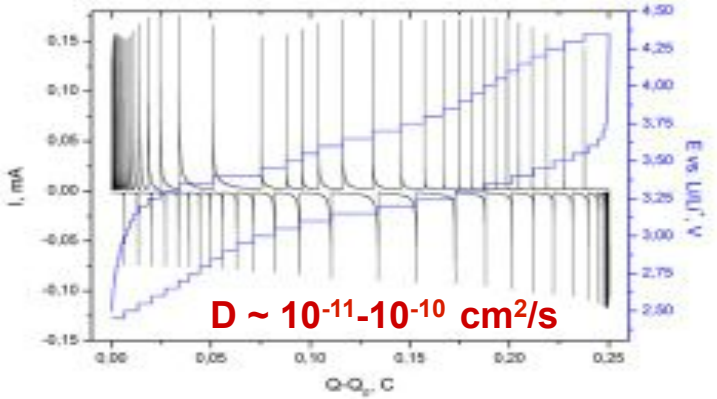




Li_2FePO_4F: новый катодный материал для литий-ионных аккумуляторов с улучшенными энергетическими параметрами





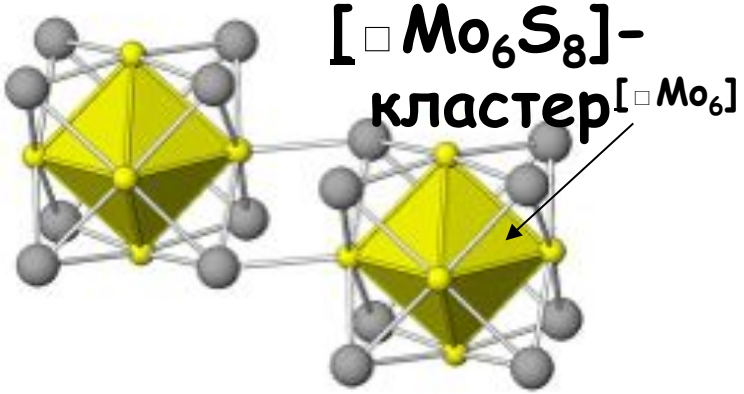


N.R. Khasanova et al., Chemistry of Materials 24 (2012), 4271

Достоинства нового материала:

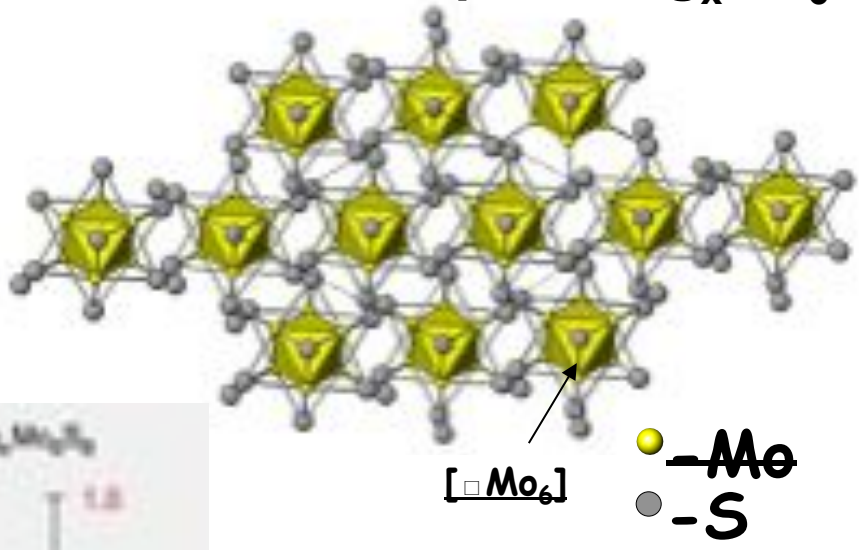
- **Минимальные объемные изменения (<2%) при зарядке/разрядке - низкая деградация при эксплуатации**
- **Однофазный механизм и высокий коэффициент диффузии ионов лития (>>1000 раз, чем у коммерческого материала $LiFePO_4$) – высокая мощность**
- **Возможность деинтеркаляции более одного иона лития – высокая энергоемкость**

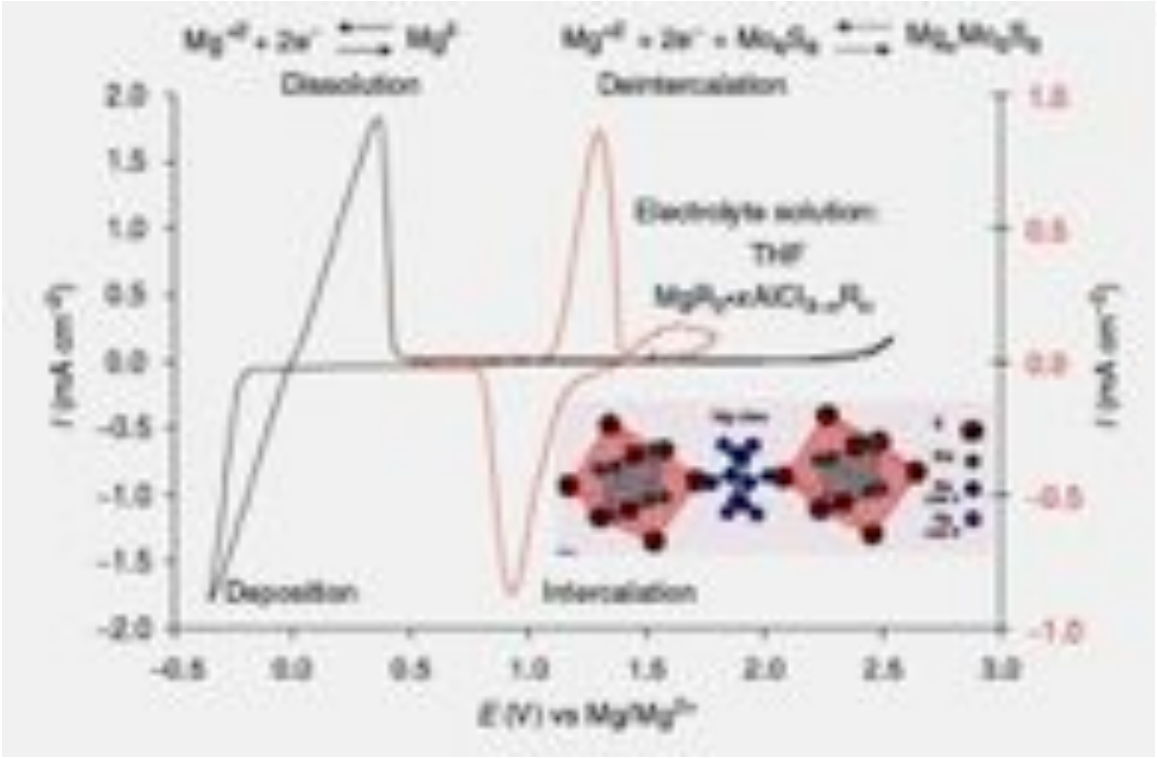
Перспективы магниевых аккумуляторов



$[\square Mo_6S_8]$-кластер

Катод: Фаза Шевреля $Mg_xMo_6S_8$



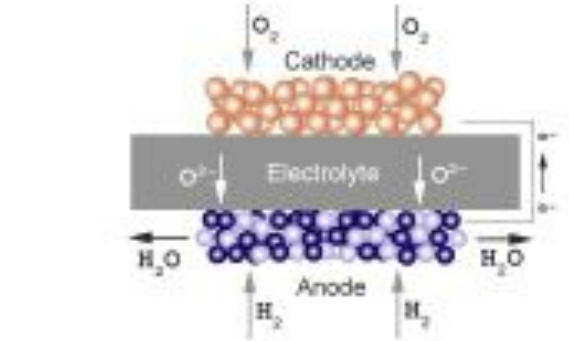


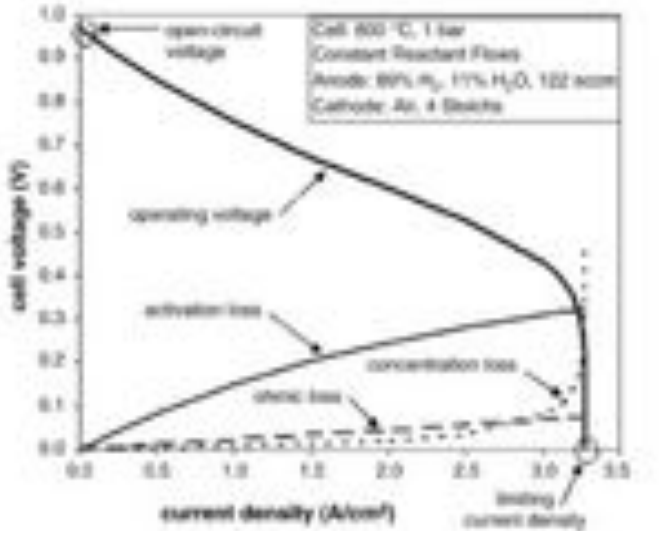
c_{max} = 122 mA·h/g

Число циклов > 2000

_D. Aurbach et al., *Nature*, 407, 2000.

Novel cathode materials for Solid Oxide Fuel Cells





$$V_{cell} = V_{open} - (V_{act} + V_{conc} + V_{ohm}) = V_{Nernst} - V_{loss}$$

M. Winter & R.J. Brodd, Chem. 104 (2004) 4245

Main requirements for cathode:

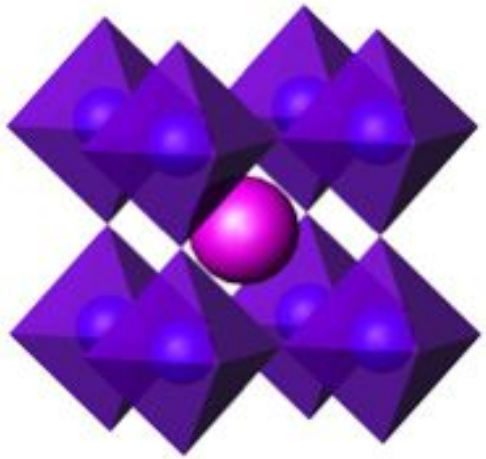
- High chemical stability (with respect to electrolyte and interconnect materials)
- High electron and oxygen-ion conductivity,
- **Thermal expansion coefficient (TEC) ± 20% of electrolyte TEC**
- **High catalytic activity for oxygen reduction**

ALS - model

$$R_{chem} = \frac{RT}{2F^2}\sqrt{\frac{\tau}{(1-\varepsilon)aC_0^2 D^* k}}$$

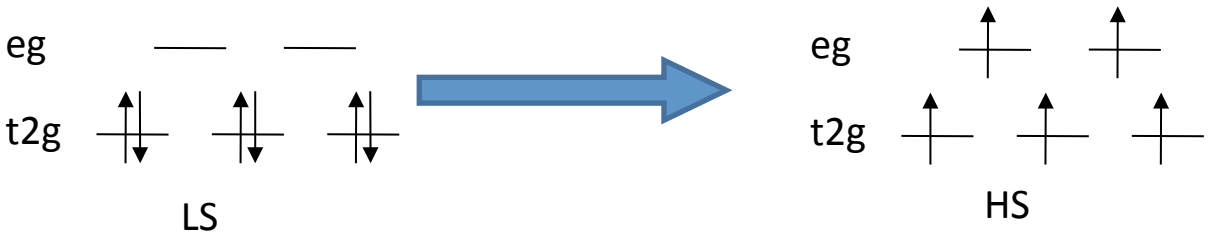
If $D^* \cdot k > 10^{-14}$ (cm^3/s^2) ⟶ activation losses are acceptable

Thermal expansion peculiarities in Co^{3+}-contained perovskites



Compound	TEC, ppmK-1
LaMnO3	10.7
La0.6Sr0.4MnO3	11.8
LaFeO3	9.5
La0.6Sr0.4FeO3	14.6
LaCoO3	24.6
La0.6Sr0.4CoO3	18
LaNiO3	13.2

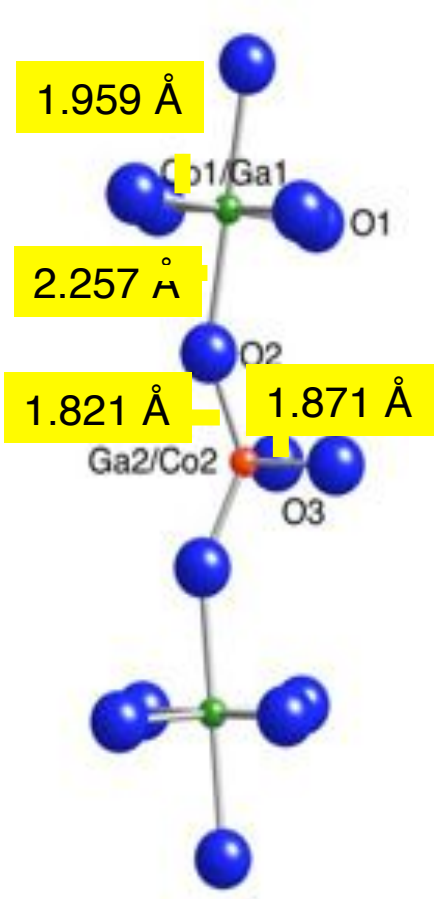
Temperature activated transitions between spin states of Co^{3+}



Q: How to solve a problem with high TEC in cobaltites?

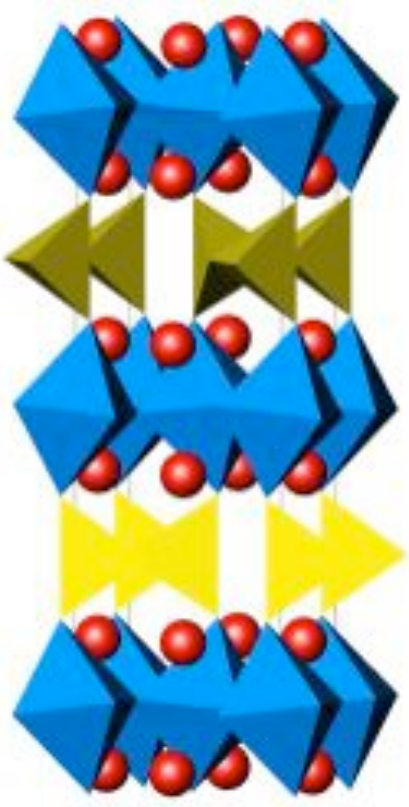
A: Choose compound with already HS Co^{3+}

Crystal structure of Sr2Co1.2Ga0.8O5 at 2K



Magnetic moment
Co^{3+}(oct) - 3.82 μB

HS Co^{3+}
both in octahedra
and tetrahedra



$Sr_2Co_2O_5$ TEC (298-623K)
11.75 ppm K^{-1}

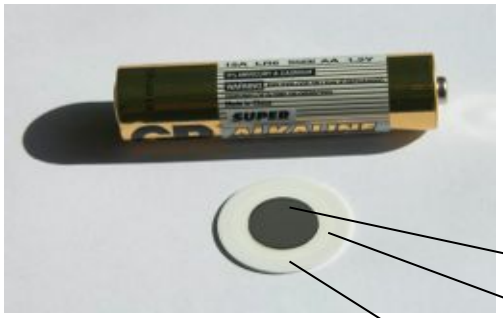
$LaCoO_3$ TEC (298-623K)
24.6 ppm K-1

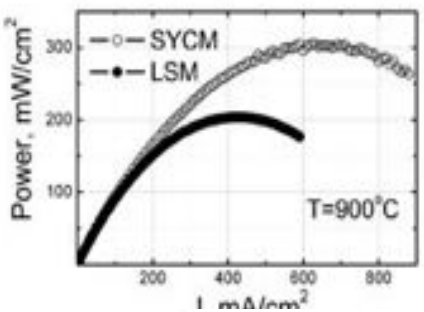
1. Кобальтсодержащие перовскиты (МГУ совместно с ИФТТ РАН)

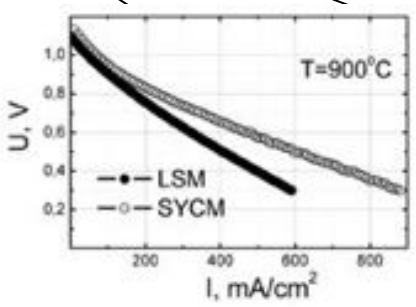
$Sr_{0.75}Y_{0.25}Co_{0.5}Mn_{0.5}O_{2.73}$ (SYCM):

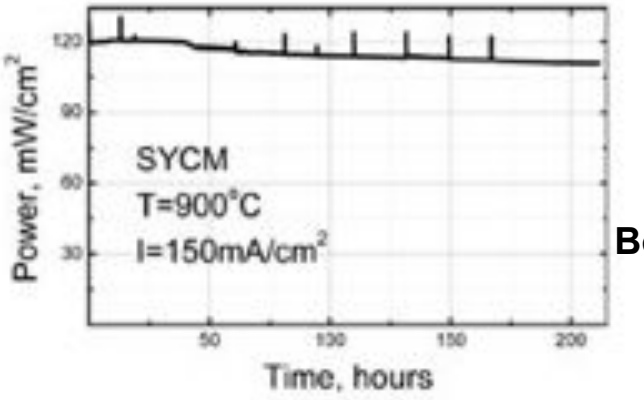
КТР=15.2 ppm K^{-1} (до 600°C – 13.3 ppm K^{-1})

σ=110 См/см (900°C)



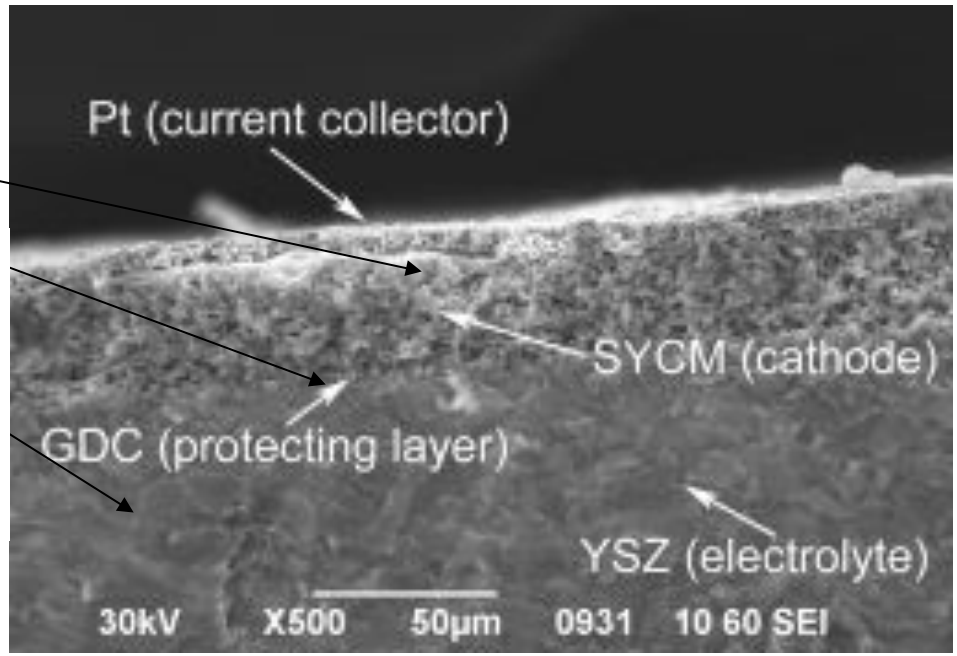






Модельные ТОТЭ:

Электролит - $ZrO_2(Y_2O_3)$ - 1500°C, 12 h (500 μm)
Анод - $NiO/CeO_2(Gd_2O_3)$ - 1300°C, 4 h (20-30 μm)
Защитный слой - $CeO_2(Gd_2O_3)$ - 1300°C, 4 h
Катод - SYCM - 1100°C, 5 h (20-30 μm).



Формирование слоев: трафаретная печать

Возможная причина деградации – «химическое» расширение

Burmistrov I. et al., J. Electrochem. Soc. 156 (2009) B1212
Drozhzhin O.A. et al. **Patent** RU 2331143 C1.

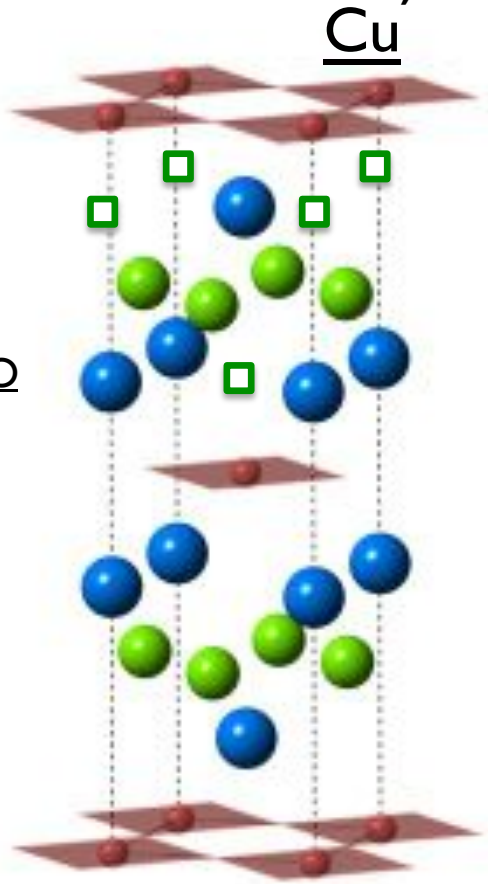
2. Слоистые купраты РЗЭ: Pr_2CuO_4 (совместно МГУ, ИФТТ РАН и FZ Juelich)

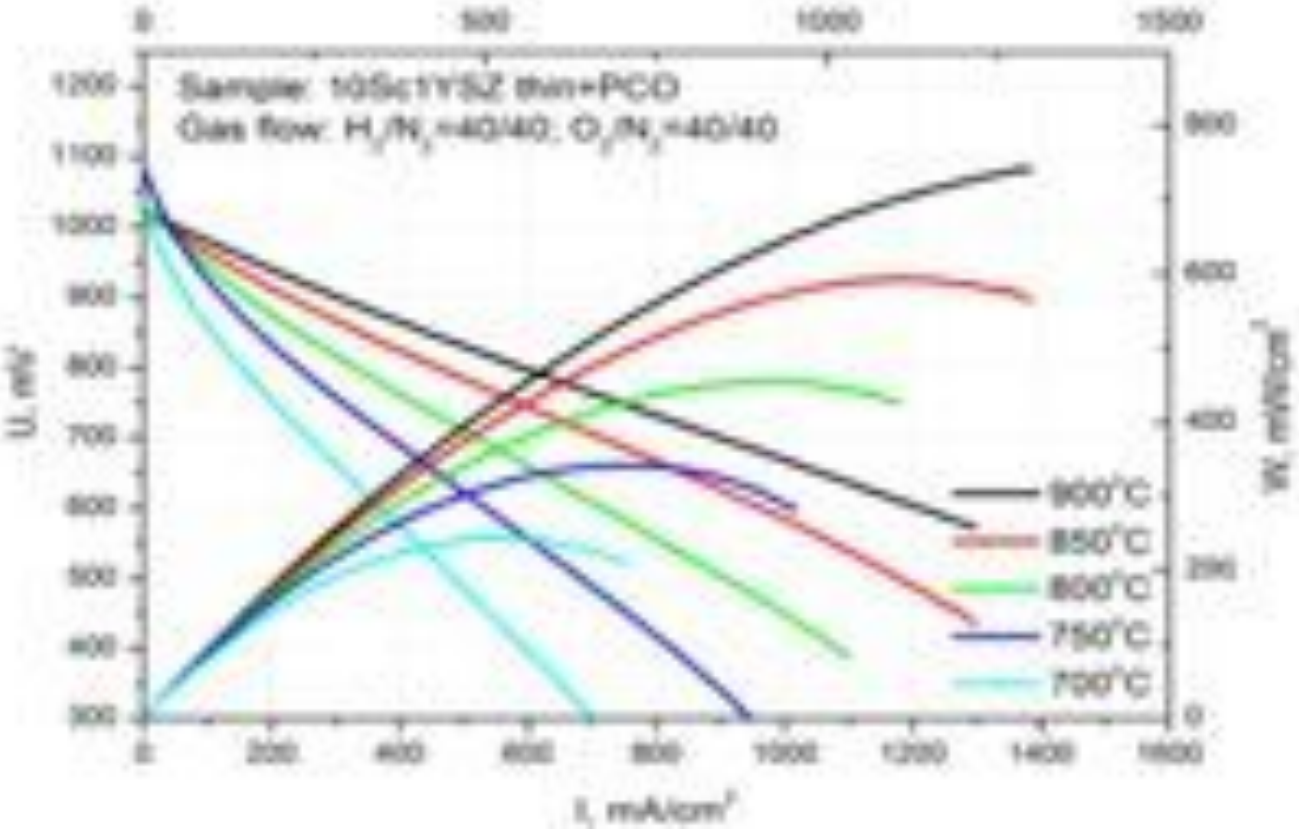
КТР=11.8 ppm K^{-1}, σ(900°C)=110 См/см; σ(600°C)=40 См/см

Диффузия кислорода в Pr_2CuO_4 (SIMS):

D* ($см^2$/сек):

LSM	~ 10^{-14}-10^{-15}	(800°C)
Pr_2CuO_4	~ 10^{-11}	(800°C)
La_2CuO_4	~ 10^{-8}	(700°C)

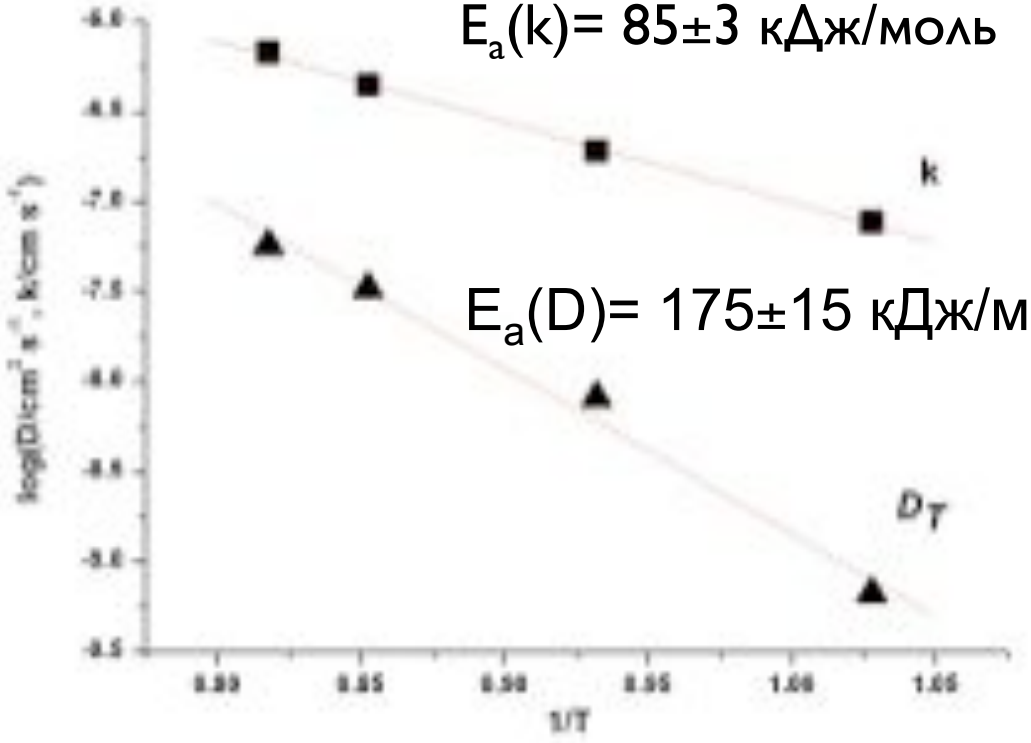




Электролит:
250 μm 10ScYSZ

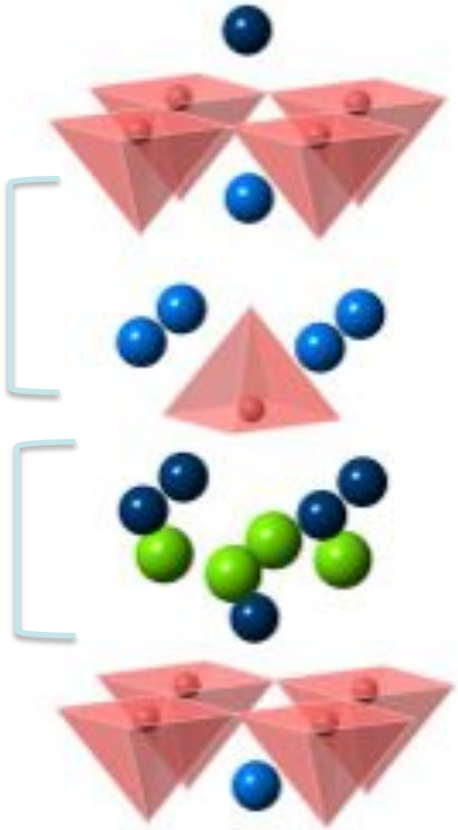
≈250 mW/cm^2 при 700°C
≈600 mW/cm^2 при 850°C

Диффузия кислорода в $Pr_{1.6}Sr_{0.4}CuO_{3.98}$ (SIMS)



$E_a(k)$= 85±3 кДж/моль

$E_a(D)$= 175±15 кДж/моль



Блок NaCl

Блок CaF_2

	La_2CuO_4	**$Pr_{1.6}Sr_{0.4}CuO_{3.98}$**	**Pr_2CuO_4**
700°C:	Блок NaCl	Блок NaCl + Блок CaF_2	Блок CaF_2
D*, см²/сек	10^{-8}	**$6{,}7\cdot10^{-10}$**	$7{,}2\cdot10^{-13}$