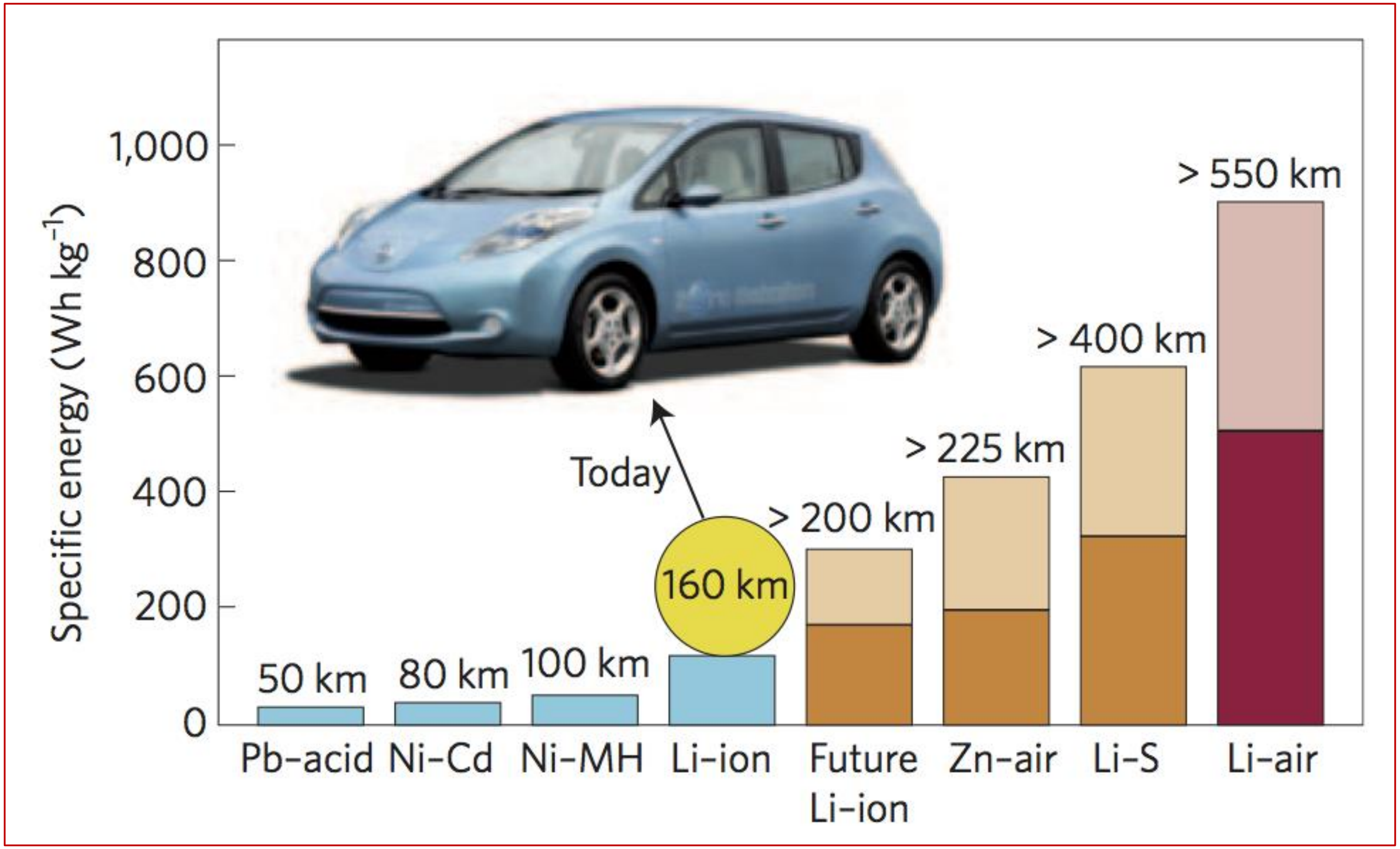
Структурные исследования электрохимических интерфейсов методами малоуглового рассеяния нейтронов и нейтронной рефлектометрии

М.В. Авдеев

Лаборатория нейтронной физики им. И.М.Франка

Объединенный институт ядерных исследований, Дубна Моск. Обл., Россия

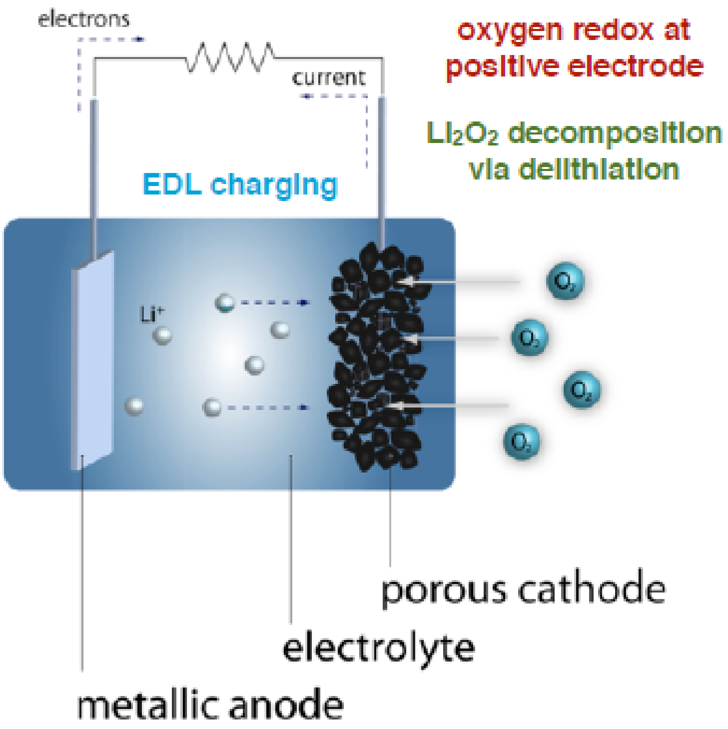
Next-Generation High-Energy and High-Power Batteries



P.G.Bruce et al. // *Nature Materials 11*(1), 2011, 19–29

Li-Air Cells

principle



theoretical voltage **2.96 V**

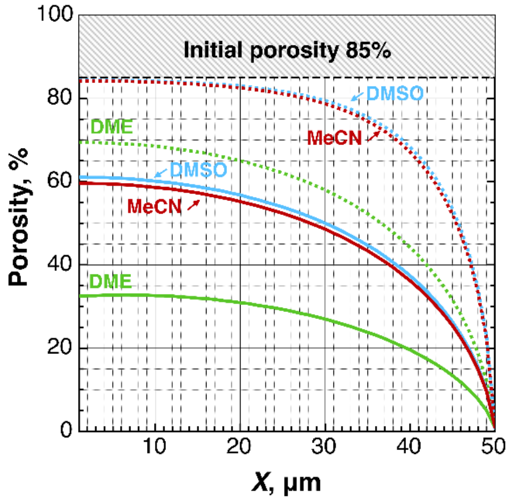
overall reaction
$2Li + O_2 \rightleftarrows Li_2O_2$

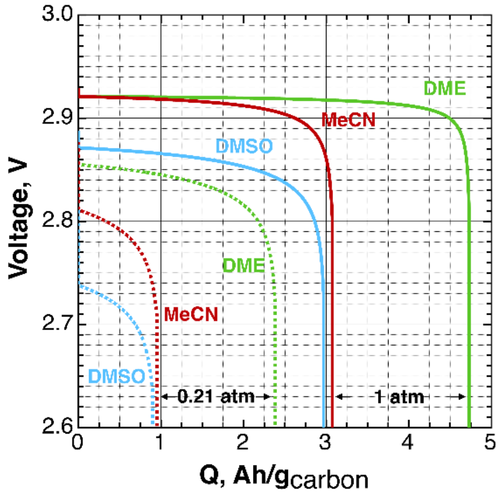
at negative electrode
$Li \rightleftarrows Li^+ + e^-$

at positive electrode
$O_2 + 2Li^+ + 2e^- \rightleftarrows Li_2O_2$

theoretical specific energy
up to **900 Wh/kg**

predictions

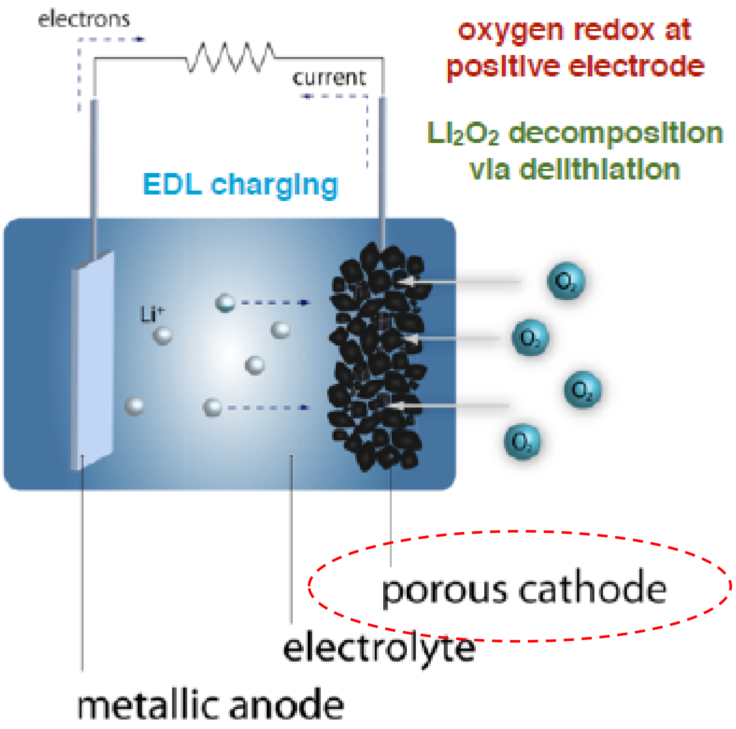




Sergeev, A. V.; Chertovich, A. V.; Itkis, D. M.; Goodilin, E. A.; Khokhlov, A. R. Effects of Cathode and Electrolyte Properties on Lithium–air Battery Performance: Computational Study. *J. Power Sources* **2015**, *279*, 707–712.

Li-Air Cells

principle



oxygen redox at positive electrode

Li_2O_2 decomposition via delithiation

EDL charging

porous cathode

electrolyte

metallic anode

theoretical voltage **2.96 V**

overall reaction
$2Li + O_2 \rightleftarrows Li_2O_2$

at negative electrode
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theoretical specific energy
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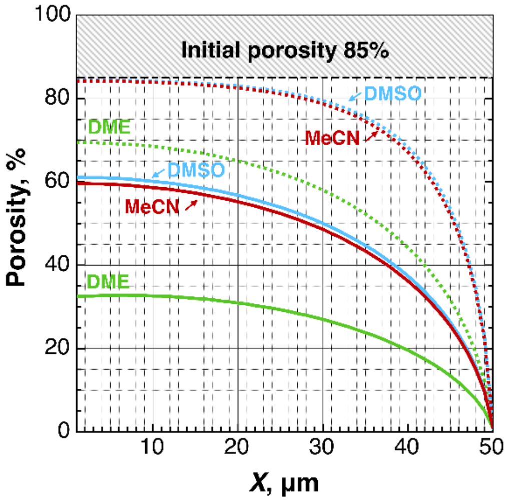
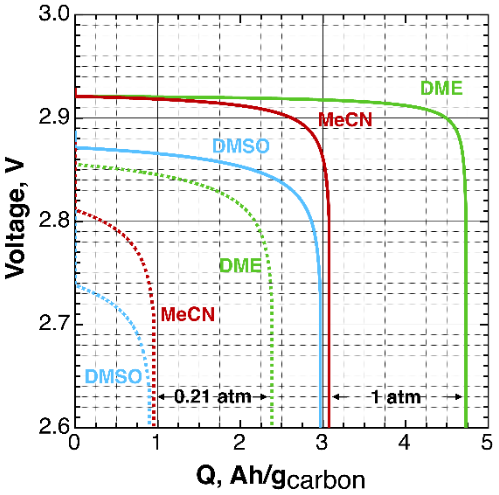
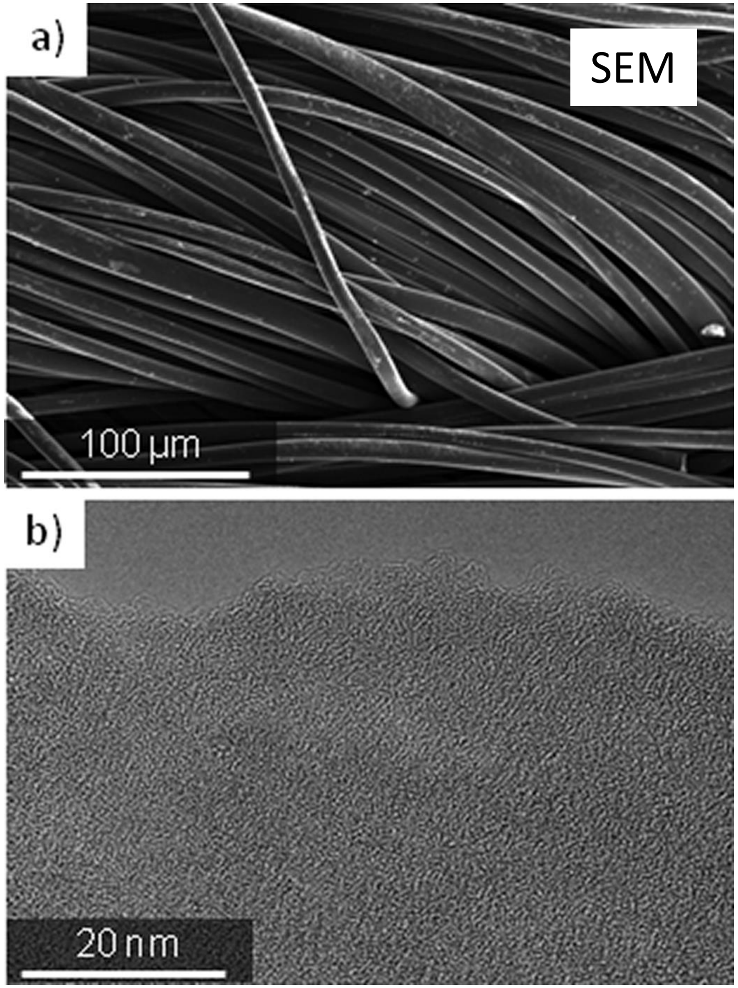
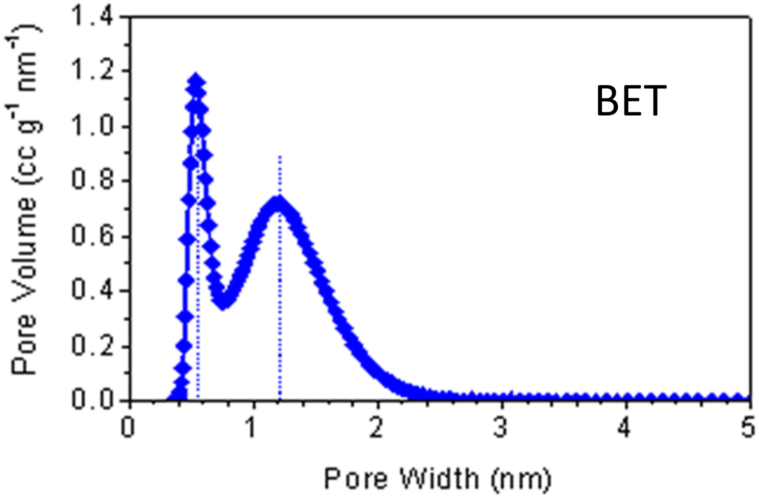


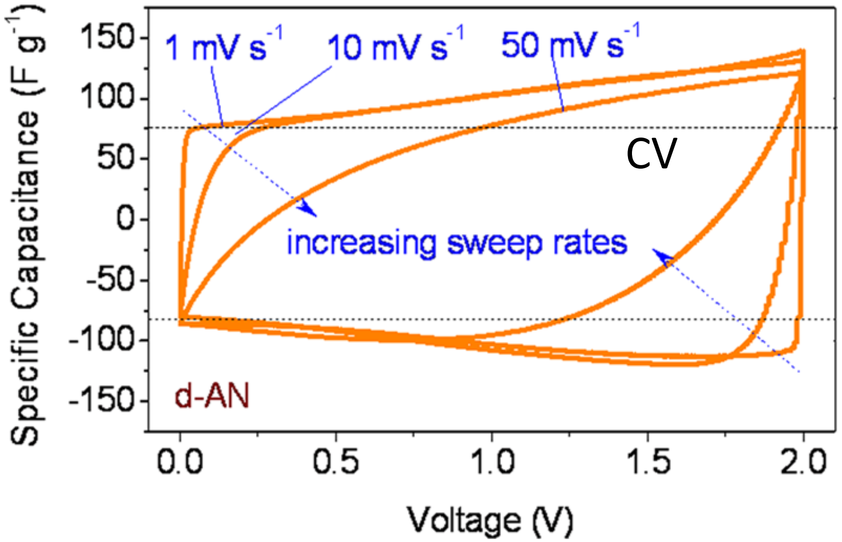


Sergeev, A. V.; Chertovich, A. V.; Itkis, D. M.; Goodilin, E. A.; Khokhlov, A. R. Effects of Cathode and Electrolyte Properties on Lithium–air Battery Performance: Computational Study. *J. Power Sources* **2015**, *279*, 707–712.

In Situ Small Angle Neutron Scattering Revealing Ion Sorption in Microporous Carbon Electrical Double Layer Capacitors







S. Boukhalfa, D. Gordon, L. He, Y. B. Melnichenko, N. Nitta, A. Magasinski, G. Yushin, *ACS Nano* **2014**, *8*, 2495–2503.

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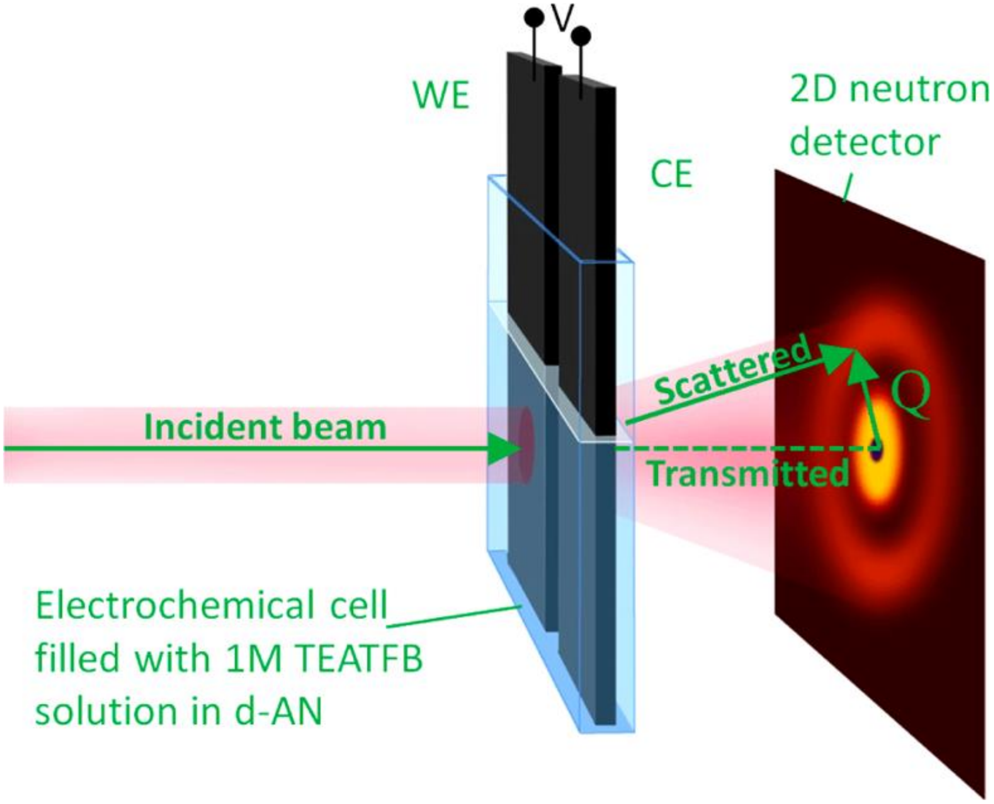
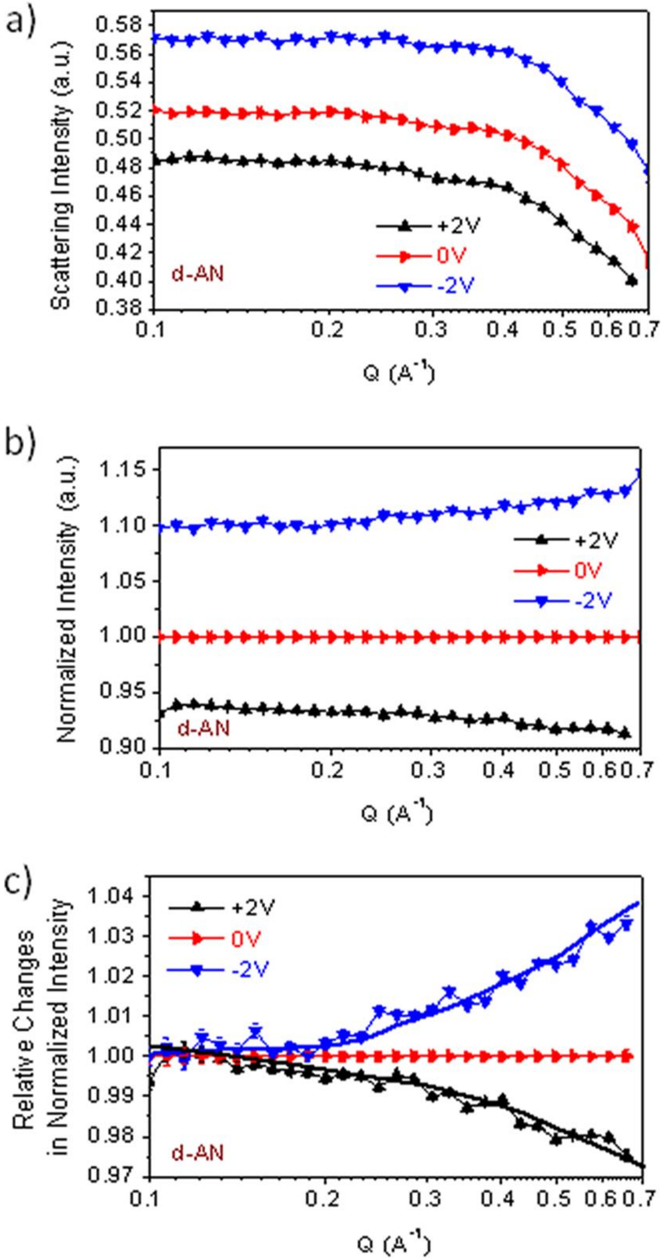
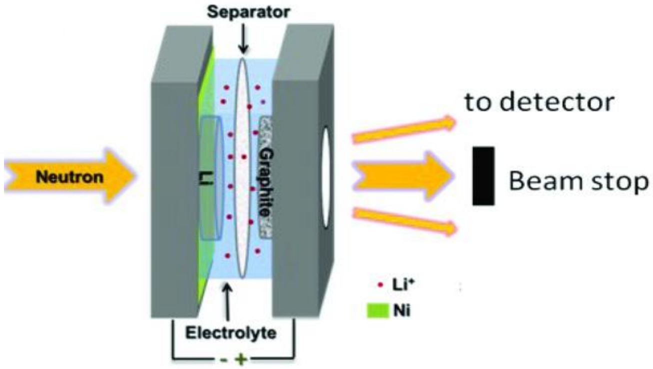
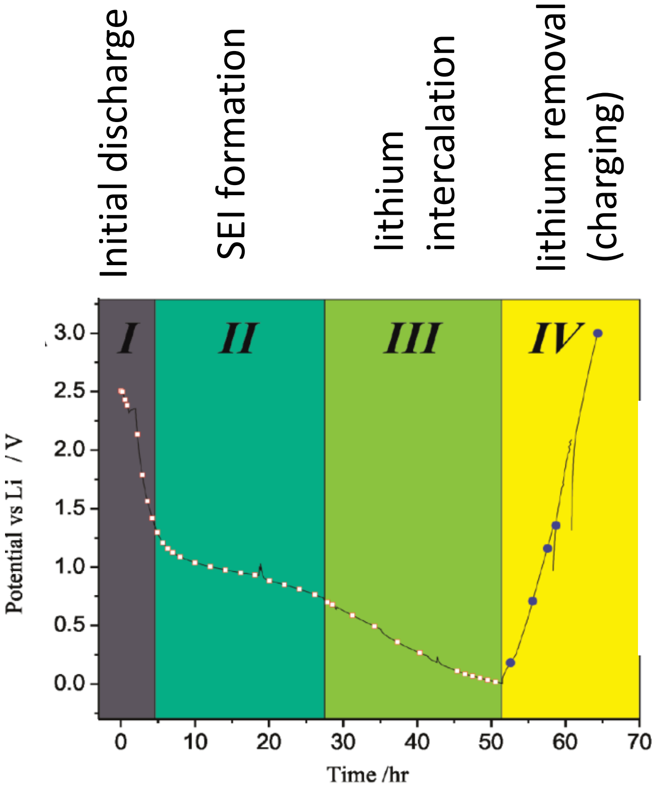


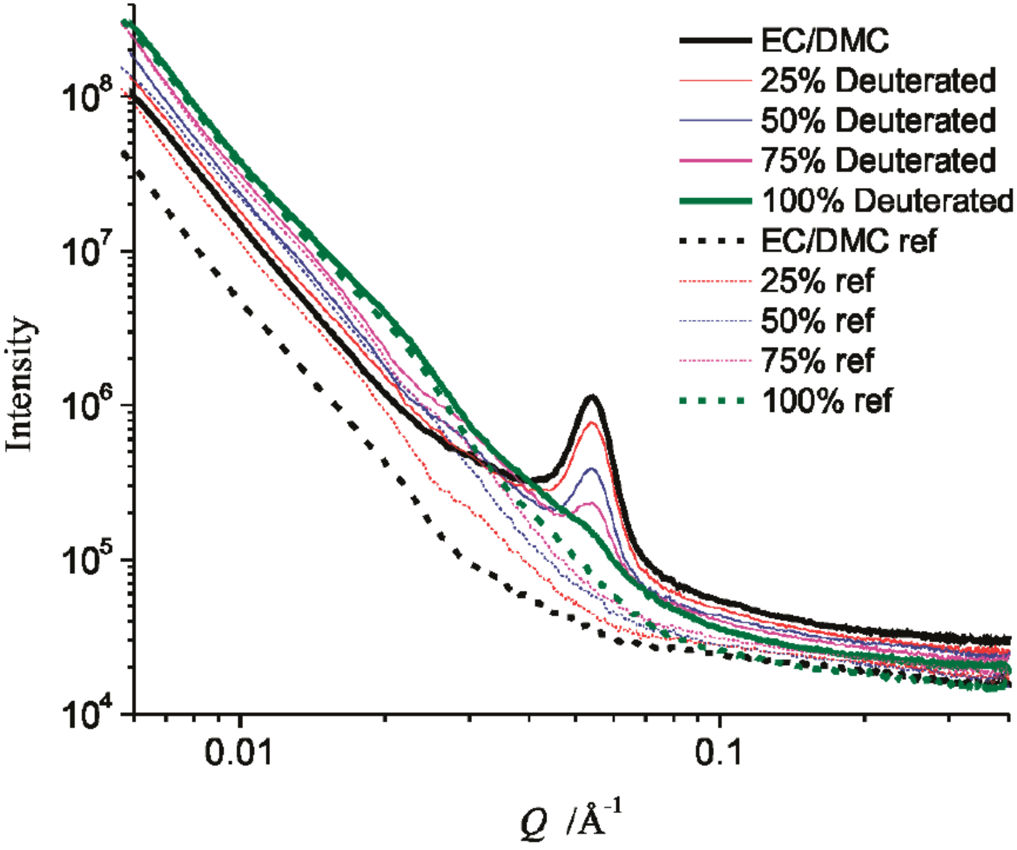


S. Boukhalfa, D. Gordon, L. He, Y. B. Melnichenko, N. Nitta, A. Magasinski, G. Yushin, *ACS Nano* **2014**, *8*, 2495–2503.

In Situ Observation of Solid Electrolyte Interphase Formation in Ordered Mesoporous Hard Carbon by Small-Angle Neutron Scattering



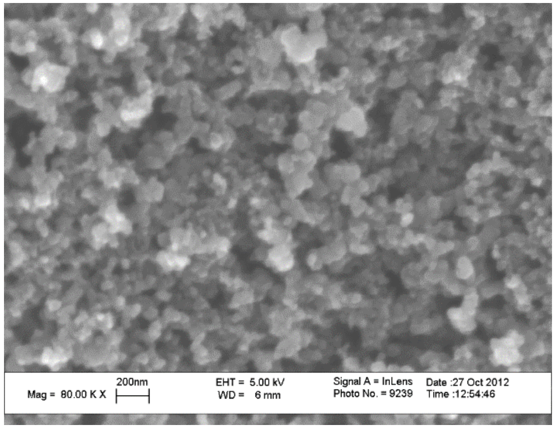




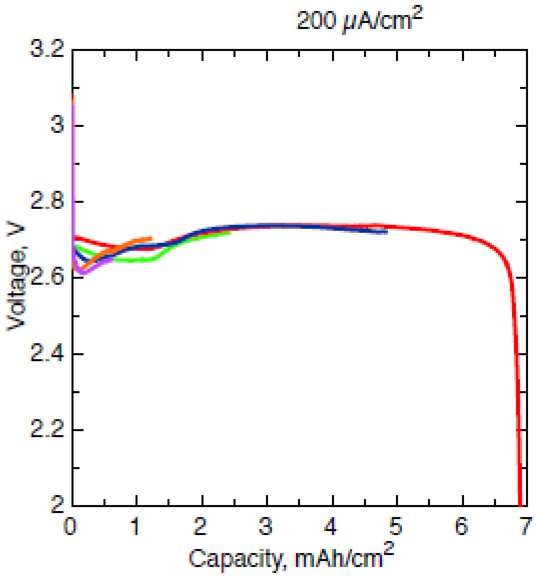
C. A. Bridges, X.-G. Sun, J. Zhao, M. P. Paranthaman, S. Dai, *J. Phys. Chem. C* **2012**, *116*, 7701–7711.

Precipitation of Lithium Peroxide in Carbon for Li-Air Batteries by SANS

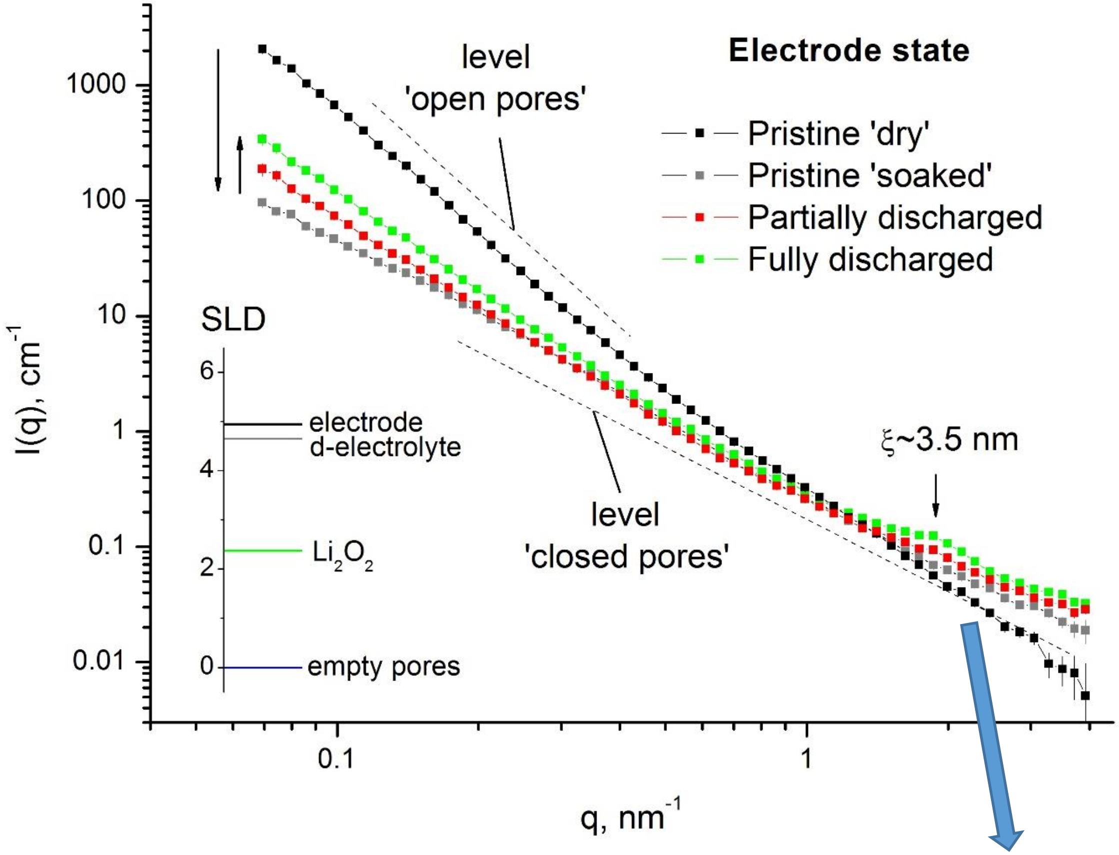
SIGRASET carbon paper

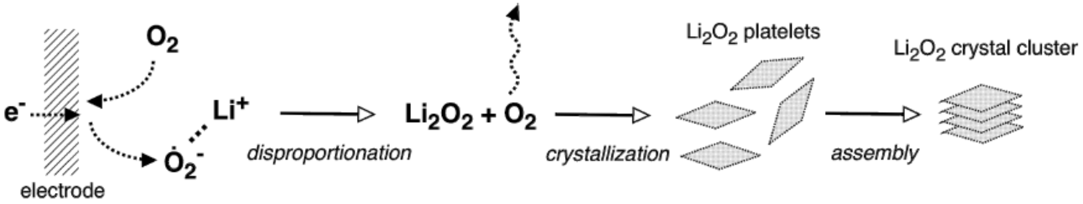


SEM Chem. Dpt. MSU



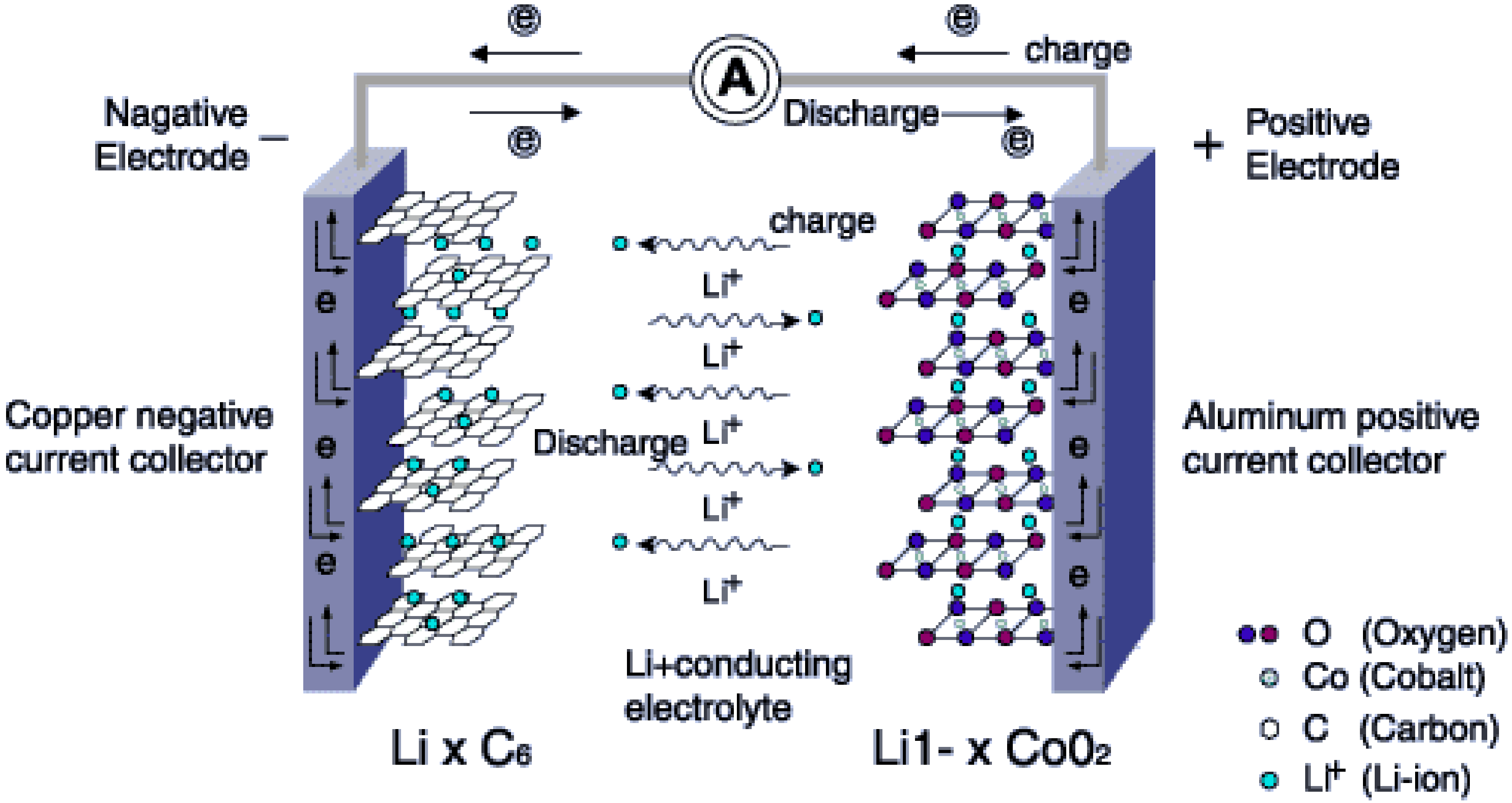
SANS, YuMO (IBR-2M)





D.M. Itkis, V.A. Vizgalov, T.K. Zakharchenko, E.Yu. Kataev, V.I.Petrenko, M.V.Avdeev, Submitted to J. Phys. Chem. Lett.

Li-Ion Batteries: Interface Structure



$$LiCo0_2 + C_6 \underset{Discharge}{\overset{charge}{\rightleftharpoons}} Li_{1-x}Co0_2 + Li_xC_6$$

Specific energy density: 100 - 250 W·h/kg

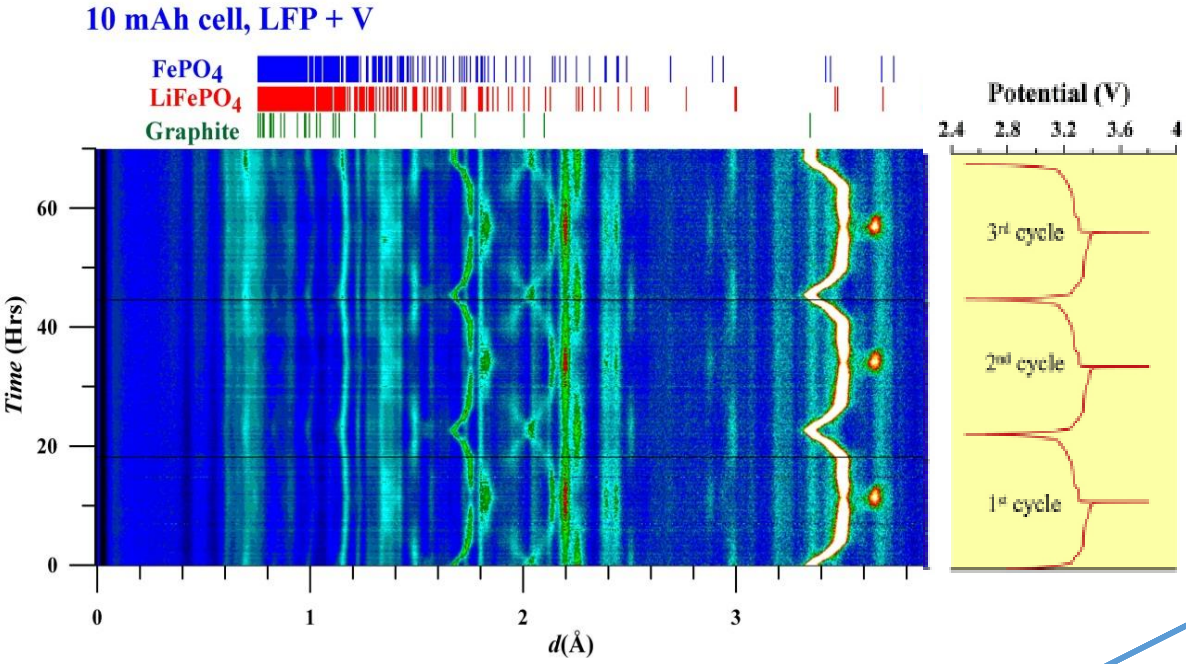
From **Gaston Narada International LTD**
http://www.gaston-lithium.com/

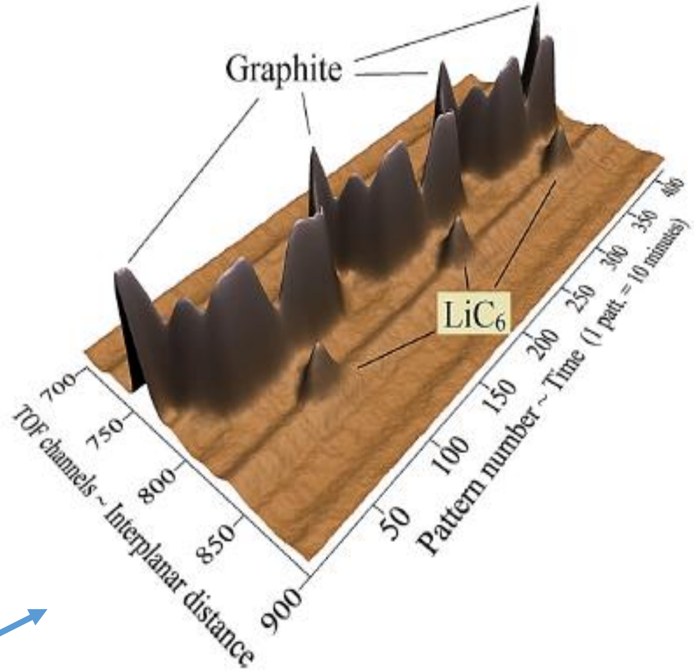
Neutron diffraction studies of electrochemical cell *in operando*

HRFD diffractometer, IBR-2 (Dubna)

Thermal mode of moderator

Evolution of neutron diffraction from lithium-based electrical current source in the process of three charging/discharging cycles (~20 hours per cycle)





olivine

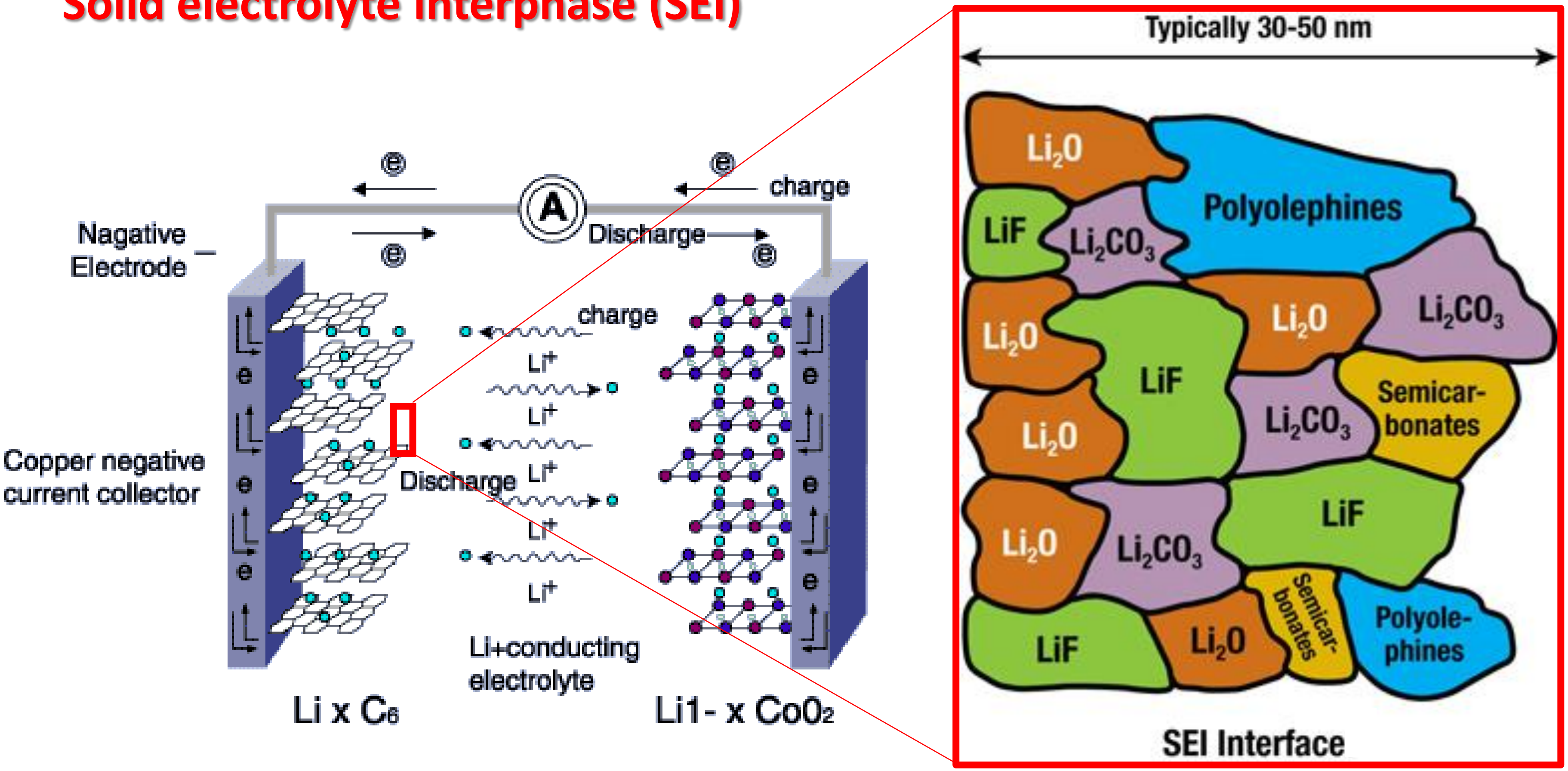
graphite

Bulk structure of electrodes

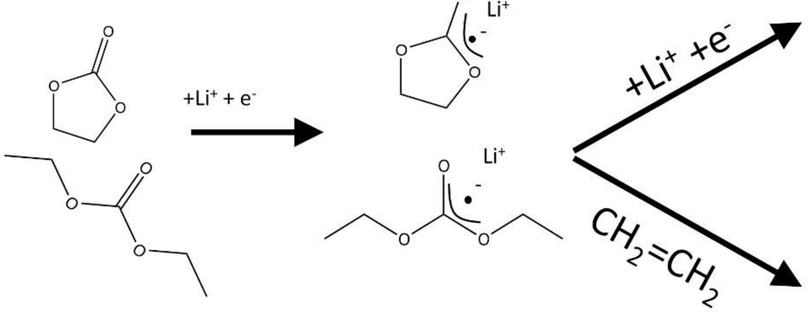
I.A.Bobrikov, A.M.Balagurov, Chih-Wei Hu, Chih-Hao Lee, Sangaa Deleg, D.A.Balagurov *J. Power Sources* 258 (2014) 356

A.M.Balagurov, I.A.Bobrikov, N.Y.Samoylova, O.A.Drozhzhin, E.V.Antipov, *Russ. Chem. Rev.* **2014**, *83*, 1120

Solid electrolyte interphase (SEI)



Solvent Reduction:



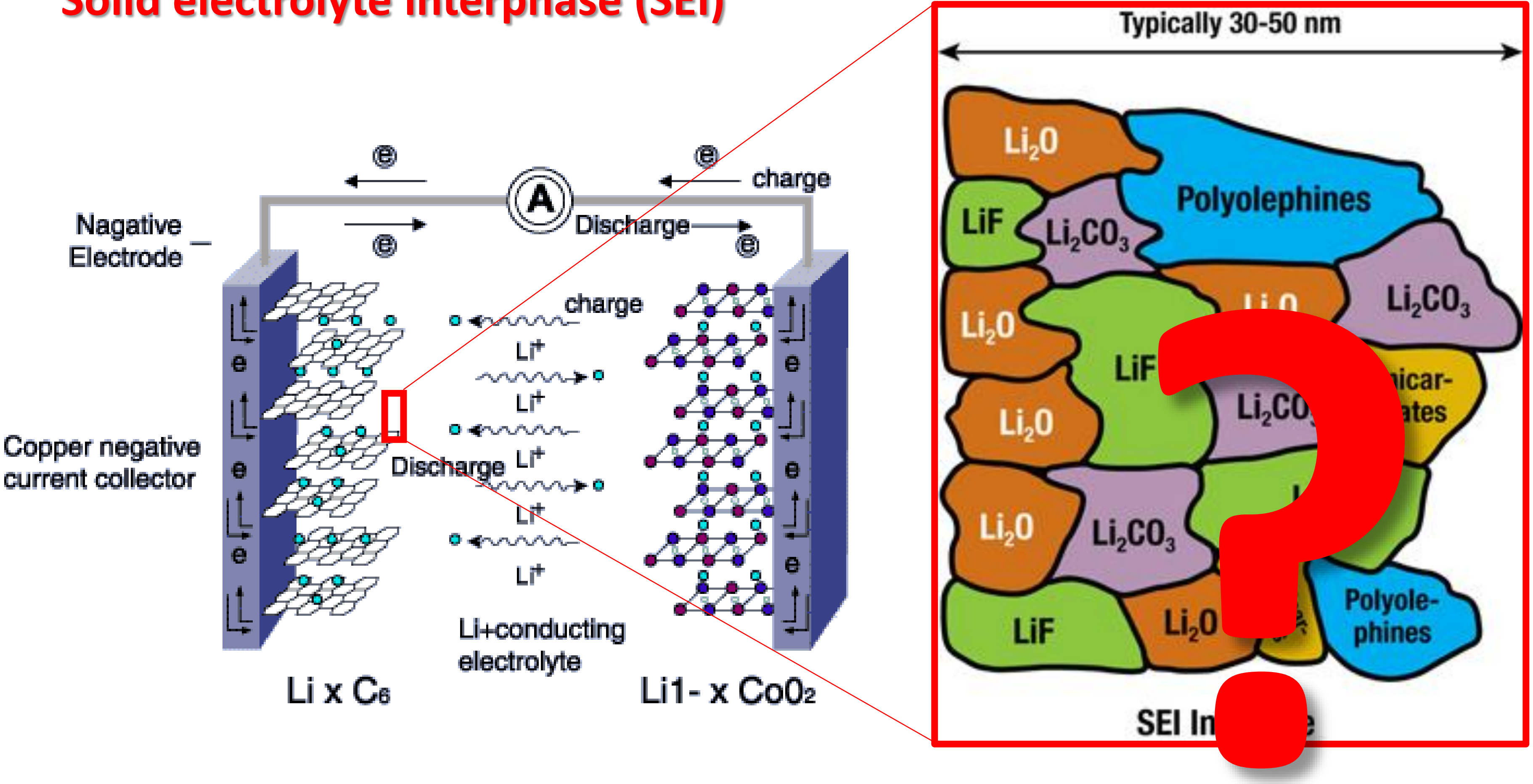
"good" SEI formation

Li_2CO_3, Li_2O, RCO_2Li, alkoxides
-compact SEI, stable,
ionically conductive

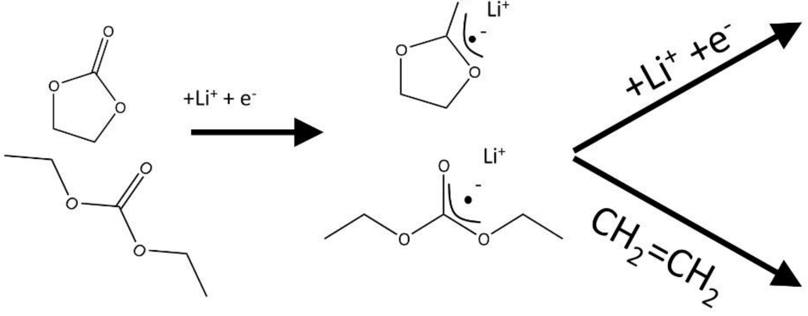
"bad" SEI formation

$(CH2OCOLi)_2$, insulating polymers
-unstable SEI, not ionically
conductive

Solid electrolyte interphase (SEI)



Solvent Reduction:



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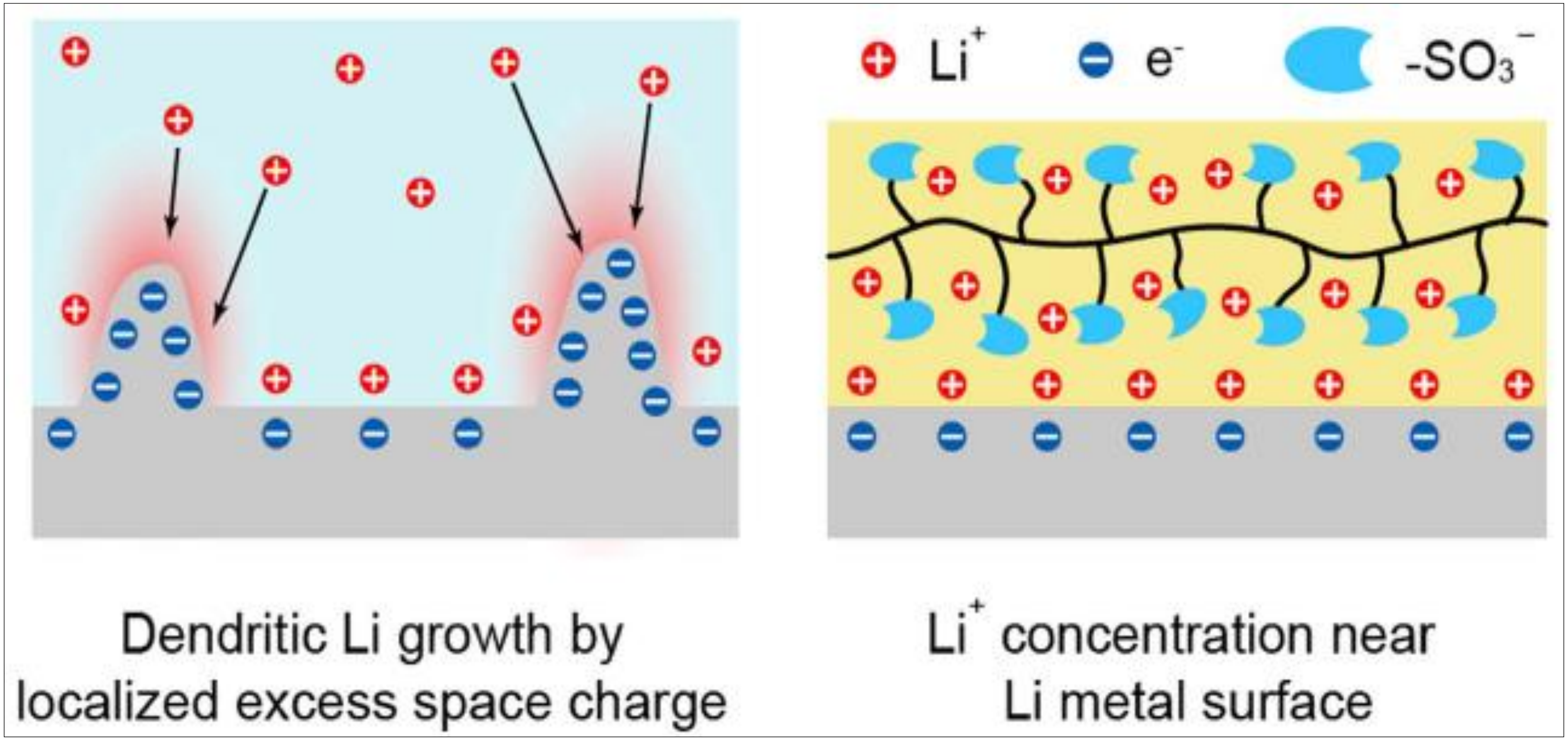
Dendride Formation in Li Deposition



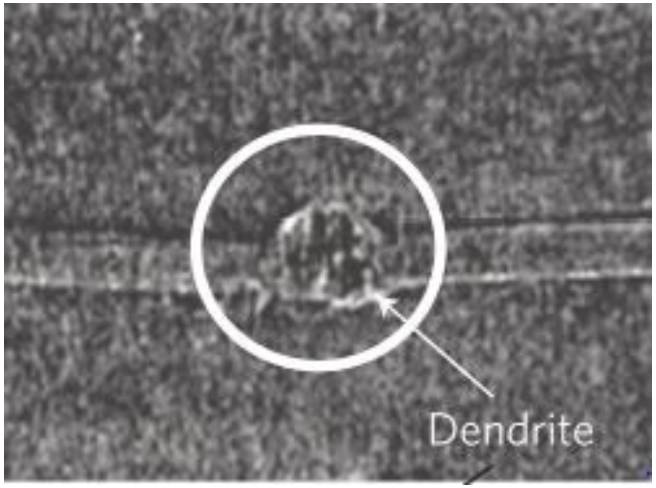
Dendritic Li growth by localized excess space charge

Li^+ concentration near Li metal surface

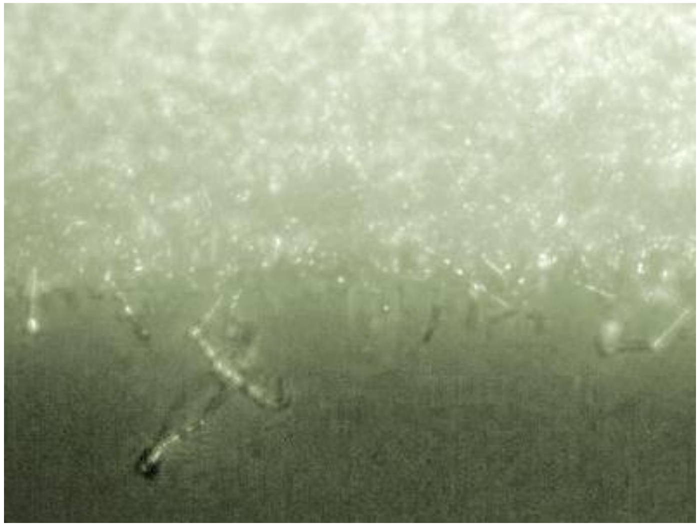
•J.L. Barton, J.O'M. Bockris.// Proc. R. Soc. Lond. A, 268, 1962, pp. 485-505.
• J.W. Diggle et al.. // J. Electrochem. Soc.11, 1969, pp. 1503-1514

Dendride Formation in Li Deposition

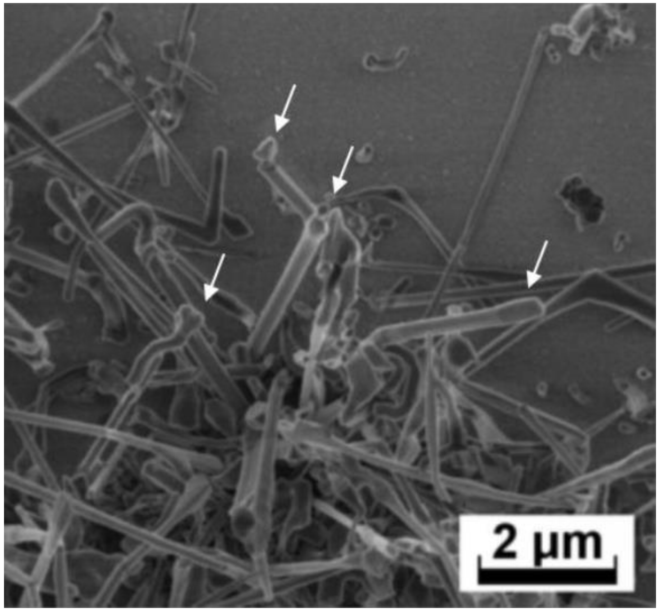
Chem. Dpt. MSU



X-ray microtomography image



Optical micrographs



SEM image of lithium dendrites

Actual lithium dendrites growing from an anode surface. Image from: R.R. Chianelli, J. Cryst. Growth, 1976, 34, 239-244.

Reflectometry studies of electrochemical interfaces

Oxidation of electrode from solution

XRR H. You, et al. *Phys. Rev. B* **1992**, *45*, 11288

NR D. G. Wiesler, C. F. Majkrzak *Physica B* **1994** , *198*, 181

Z. Tun, et al. *J. Electrochem. Soc.* **1999**, *146*, 988

P. M. Saville, et al. *J. Phys. Chem. B* **1997**, *101*, 1

S. Singh, et al. *Corrosion Sci.* **2009**, *51*, 575

Intercalation of metals into electrode from solution

XRR M. Hirayama, et al. *Electrochem. Acta* **2007**, *53*, 871;
M. Hirayama, et al. *J. Power Sources* **2007**, *168*, 493;
M. Hirayama, et al. *J. Electrochem. Soc.* **2007**, *154*, A1065

XRR/NR M. Hirayama, et al. *Electrochemistry* **2010**, *78*, 413

NR B. Jerliu, et al *J. Phys. Chem. C* **2014**, *118*, 9395

B. Jerliu, et al. *Phys. Chem. Chem. Phys.* **2013**, *15*, 7777

M. Wagemaker, et al. *Physica B* **2003**, *336*, 124

J. F. Browning, et al. *ACS Appl. Mater. Interfaces* **2014**, *6*, 18569

Solvation of polymer-based electrodes

NR R. W. Wilson, et al. *PCCP.* **1999**, *1*, 843

J. M. Cooper, et al. *JACS* **2004**, *126*, 15362

A. Glidle, et al. *Langmuir* **2009**, *25*, 4093

EDL in ionic liquid

NR Y. Lauw, et al. *Langmuir* **2012**, *28*, 7374

Hydrogen adsorption in electrode

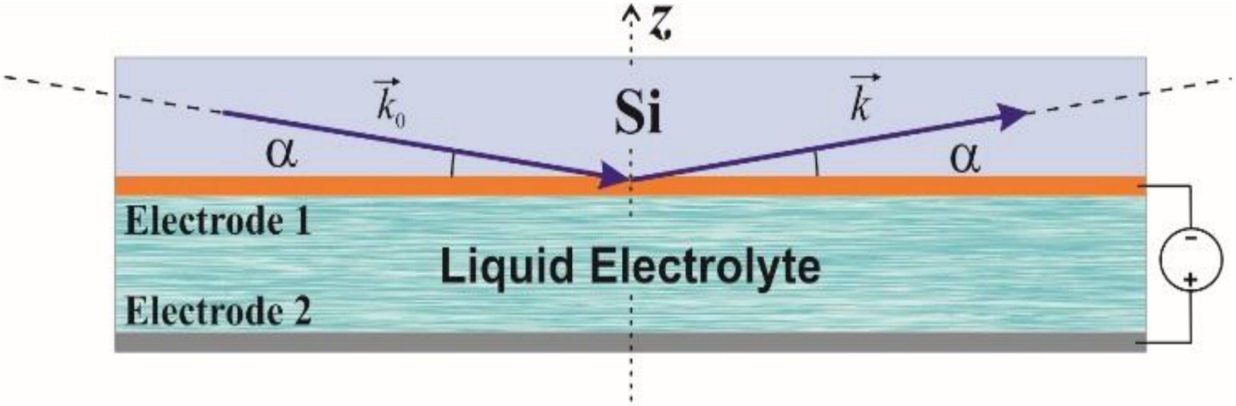
NR M. Vezvaie, et al. *J. Electrochem. Soc.* **2013**, *160*, C414

Liquid-liquid metal interface

XRR L. Bosio *J. Electrochem. Soc.* **1992**, *139*, 2110

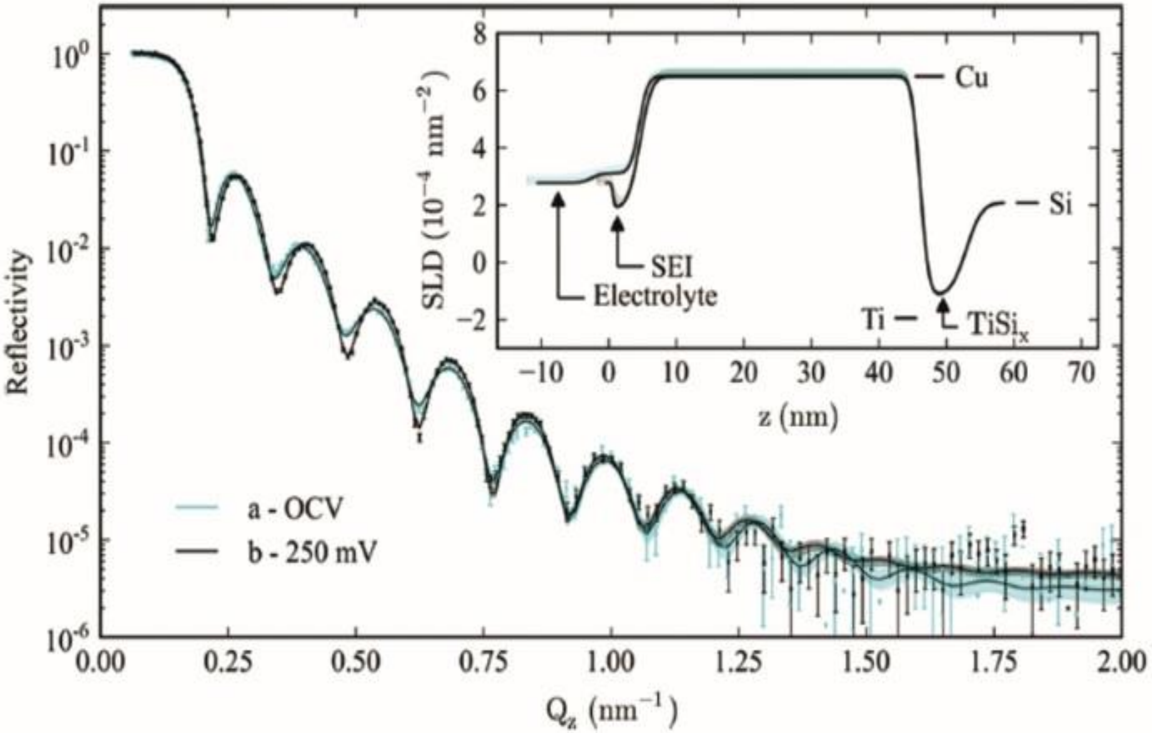
D.M. Itkis, J.J. Velasco-Velez, A. Knop-Gericke, A. Vyalikh, M.V. Avdeev, L.V. Yashina, Probing of electrochemical interfaces by photons and neutrons in operando. Review *ChemElectroChem* 2 (2015) 1427

In-Situ NR Studies of SEI Formation



Scheme of NR experiment with electrochemical interface

V = 0 – 6 V



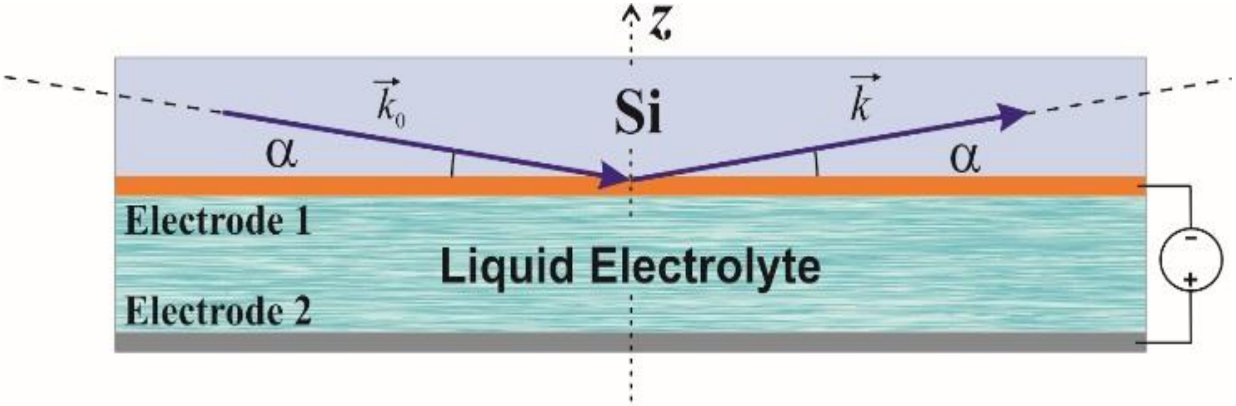
Characterization of SEI in 50% d-EC-DEC-LiPF$_6$/Cu

SLD: 10-20% lower than that of electrolyte;
thickness of 4 – 8 nm

EC - ethylene carbonate
DEC - diethyl carbonate

J. E. Owejan, J. P. Owejan, S. C. DeCaluwe, J. A. Dura, *Chem Mater* **2012**, *24*, 2133–2140

In-Situ NR Studies of SEI Formation



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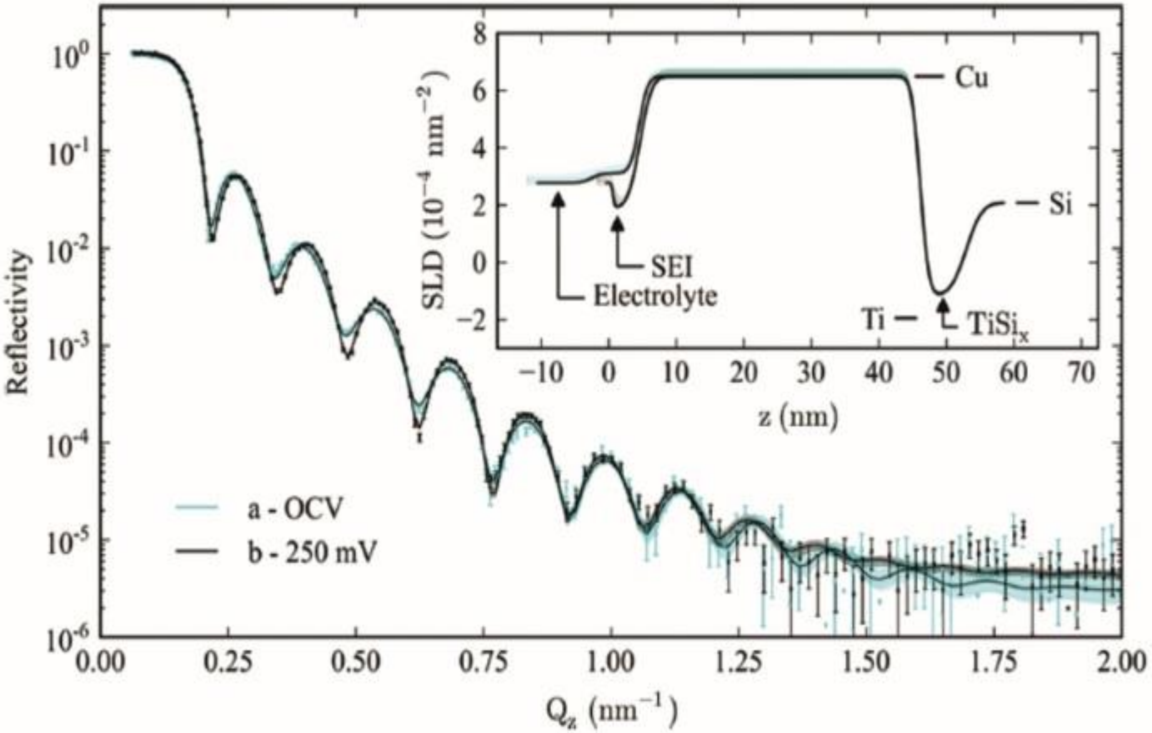

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Good model electrode
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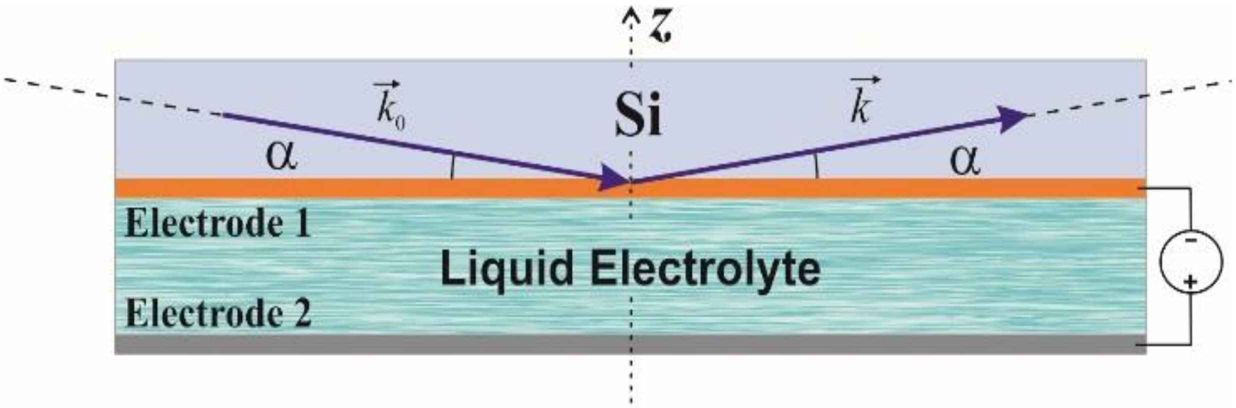
In-Situ NR Studies of SEI Formation



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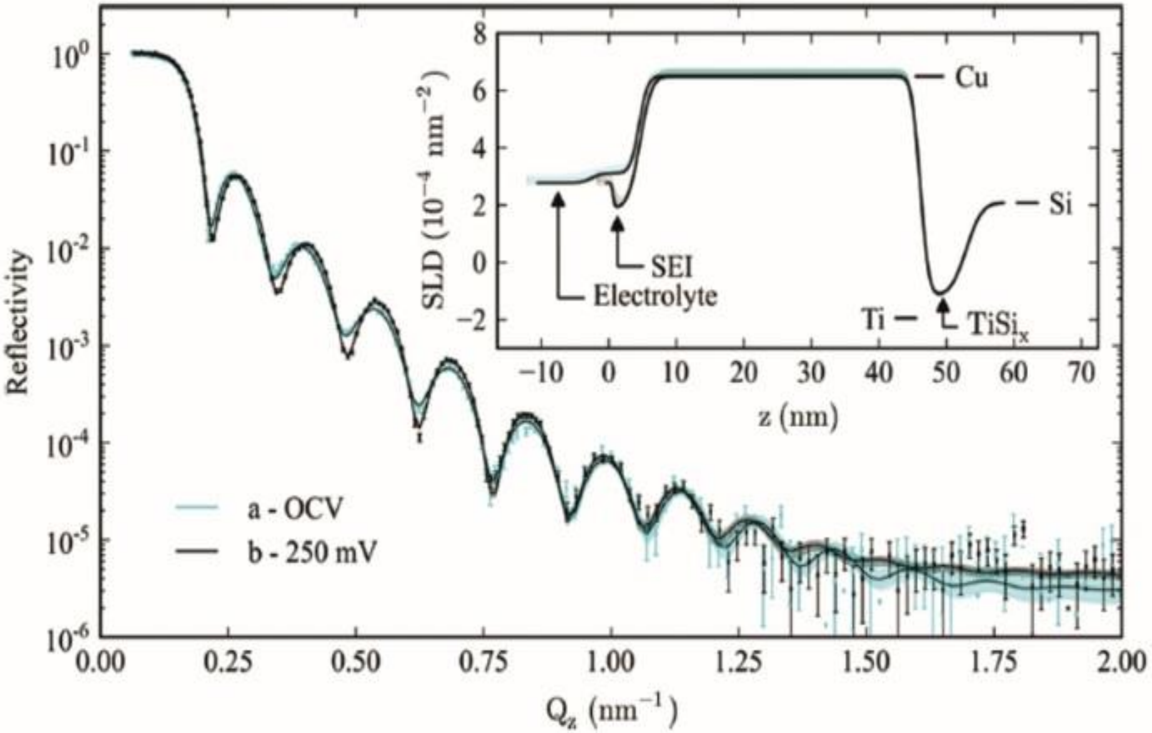

Matching of Si substrate

Characterization of SEI in 50% d-EC-DEC-LiPF$_6$/Cu

SLD: 10-20% lower than that of electrolyte;
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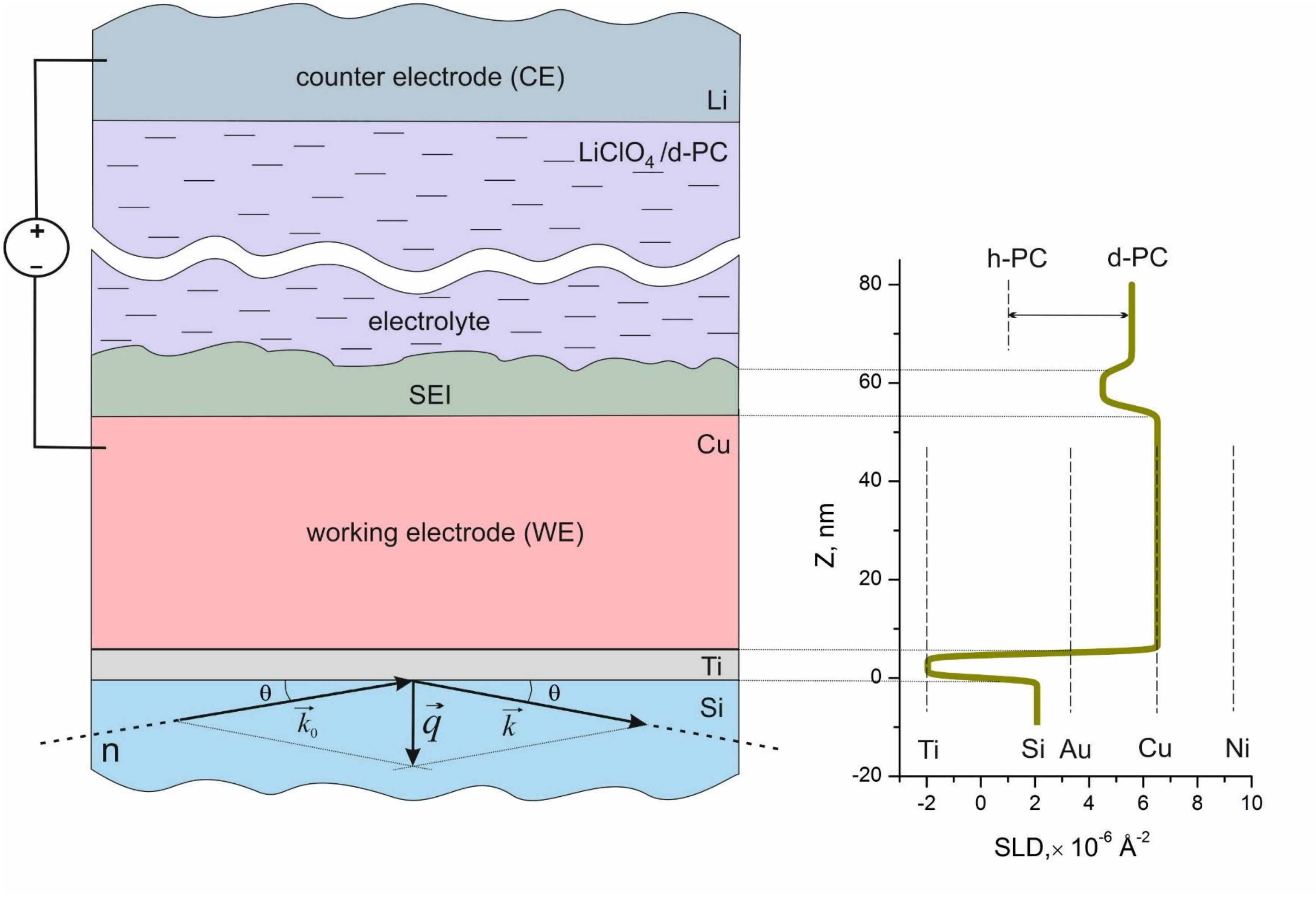
Good model electrode
- no Li intercalation

J. E. Owejan, J. P. Owejan,
S. C. DeCaluwe, J. A. Dura,
Chem Mater **2012**, *24*, 2133–2140

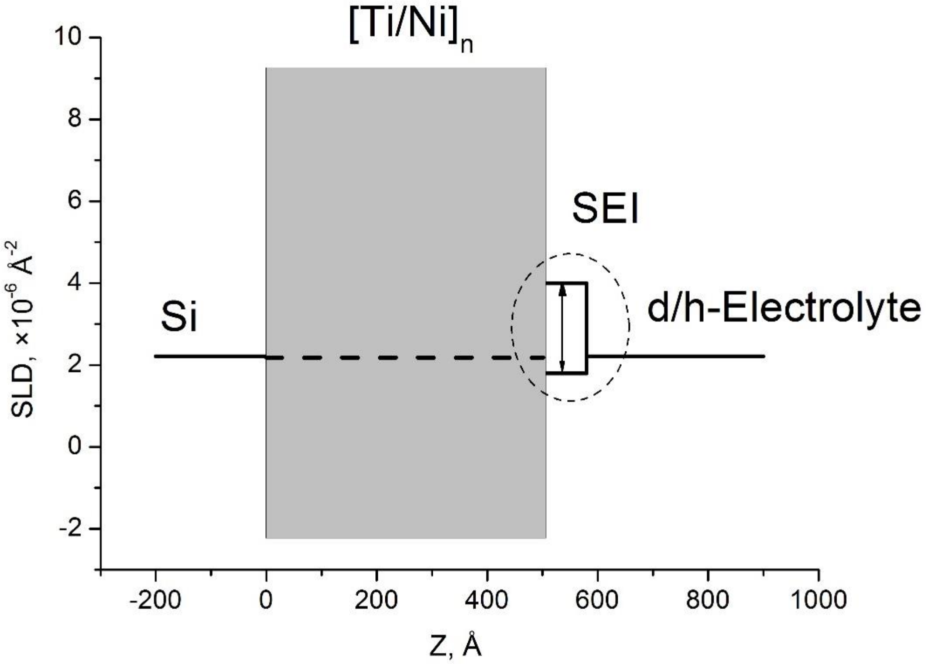
SEI detection by NR: choice of electrode material

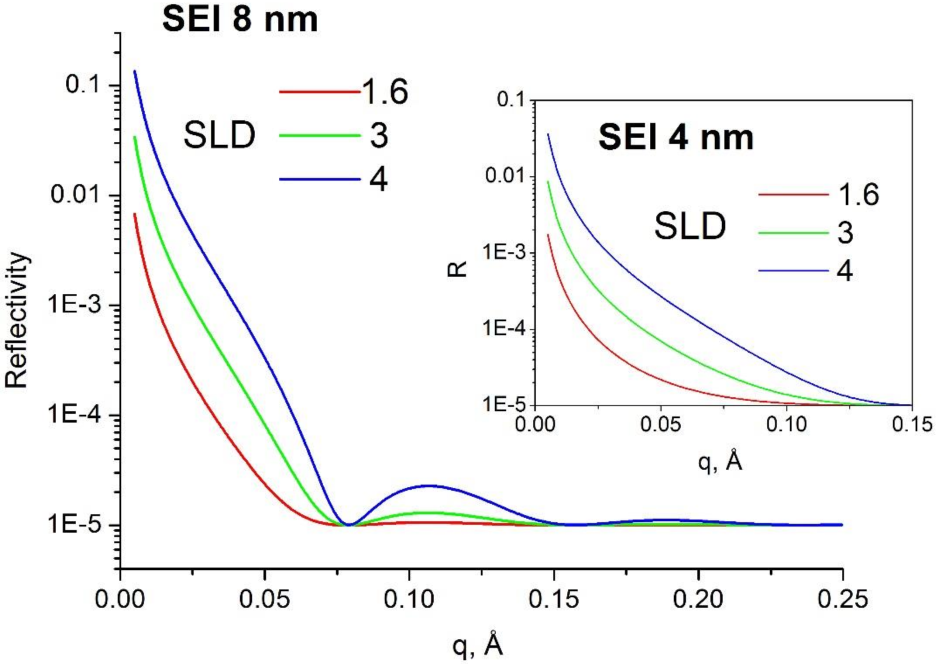


Full matching of substrate

Calculations

Electrode





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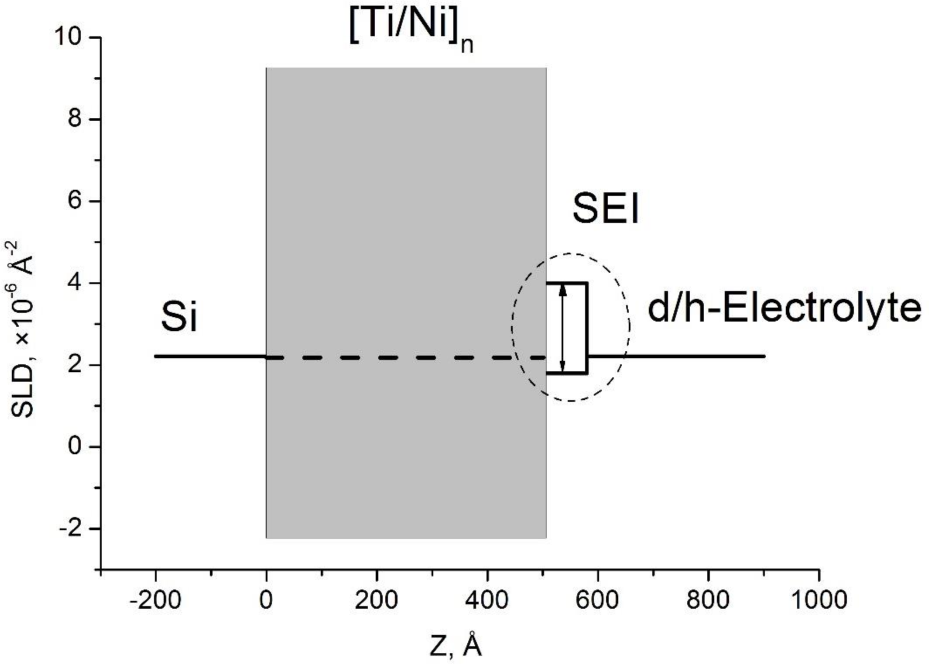
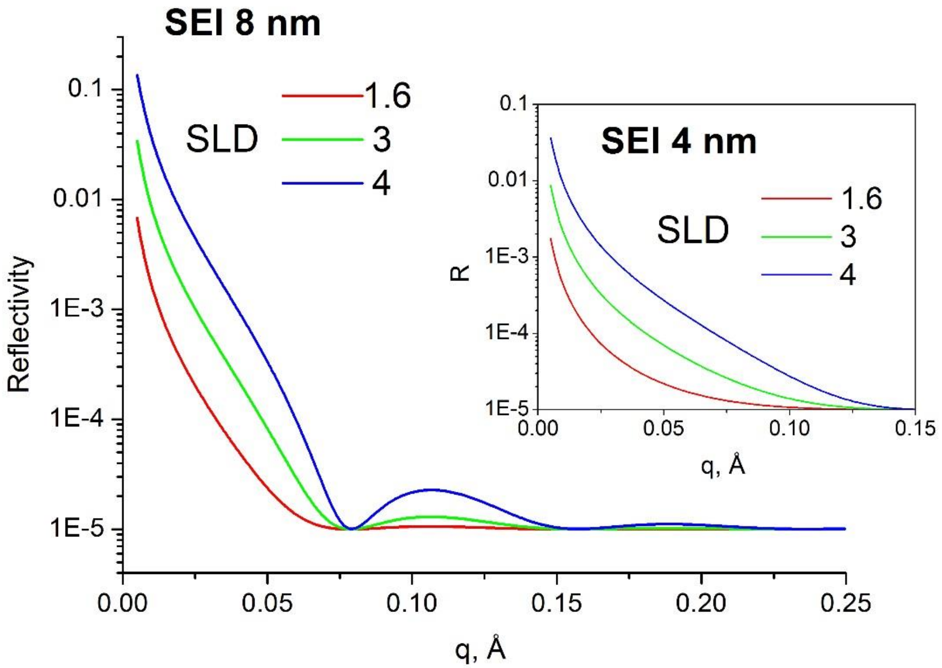


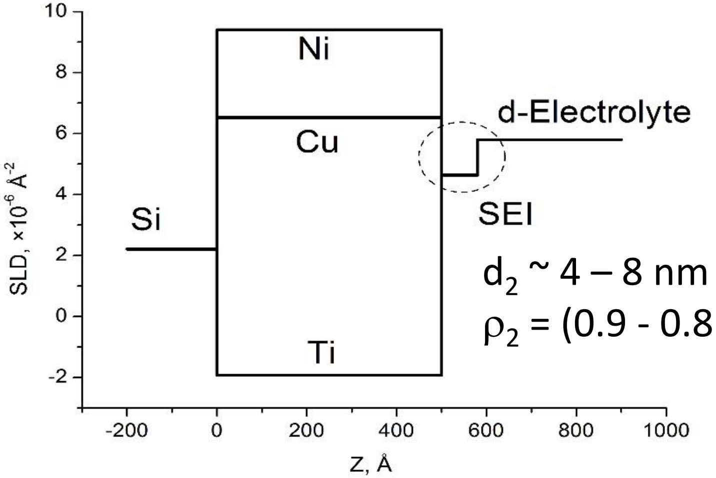


Difficult realization of strictly homogeneous structure with required SLD

Single metal layer: probing of different materials

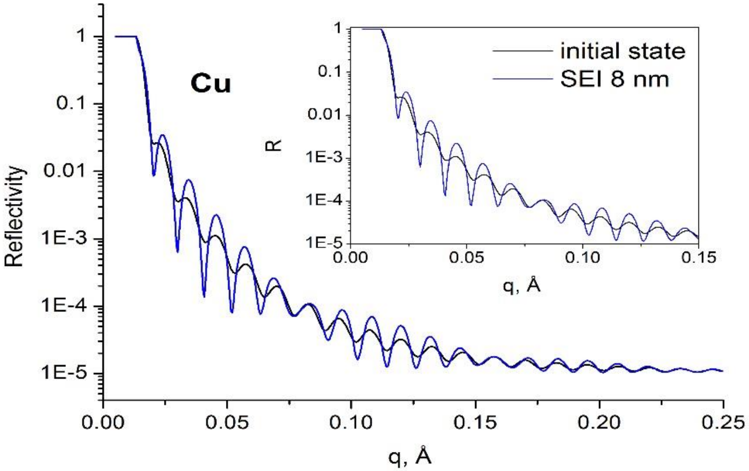
Calculations

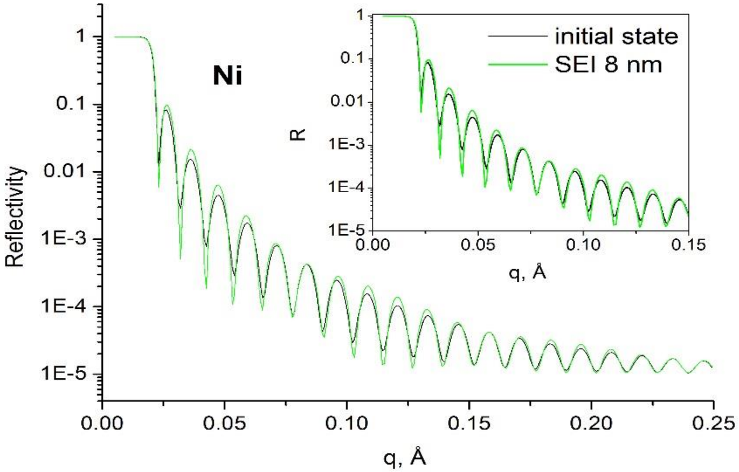
Electrode

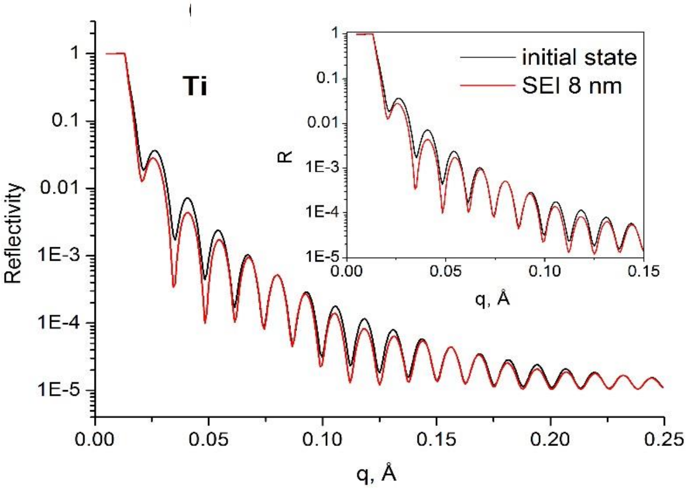


d_2 ~ 4 – 8 nm

$\rho_2 = (0.9 - 0.8)\ \rho_3$

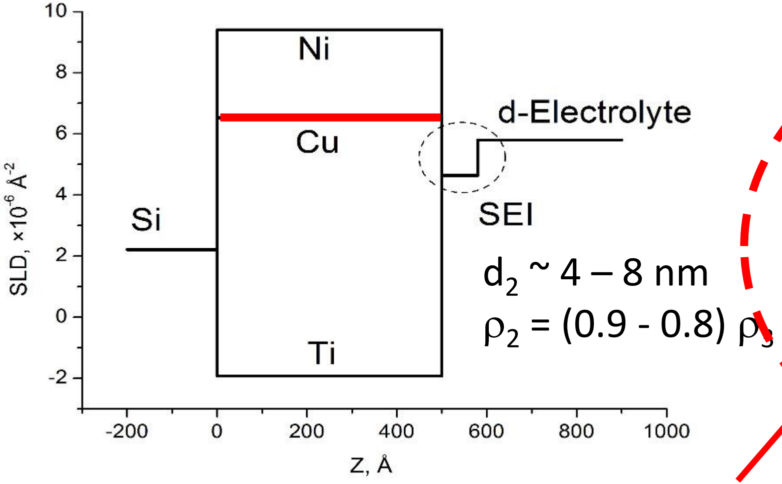




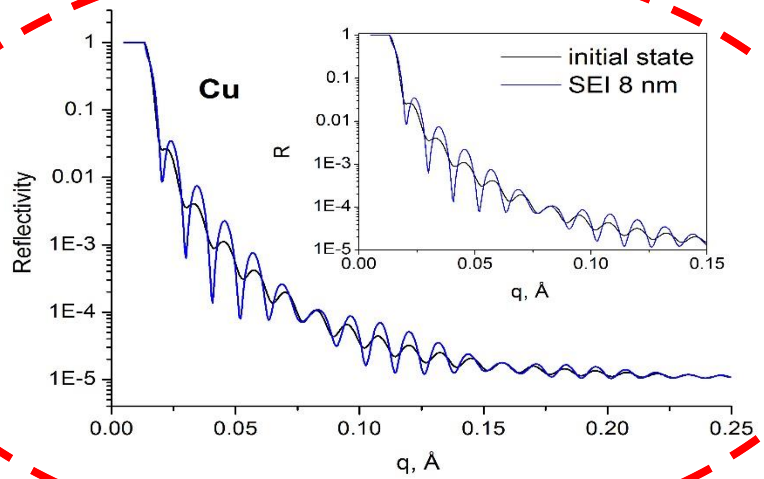


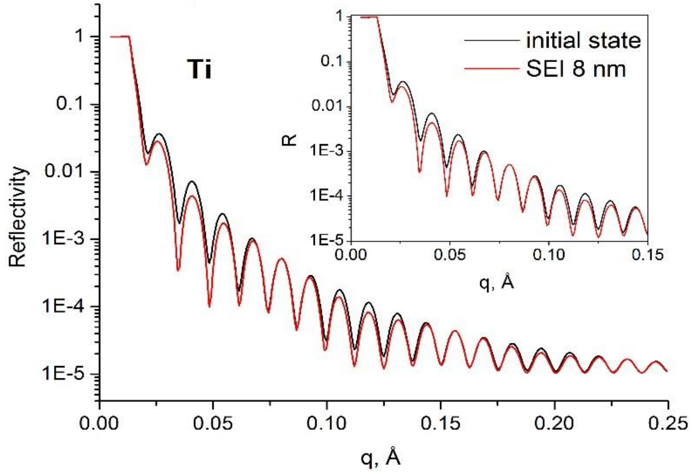
Single metal layer: probing of different materials

Electrode



Calculations



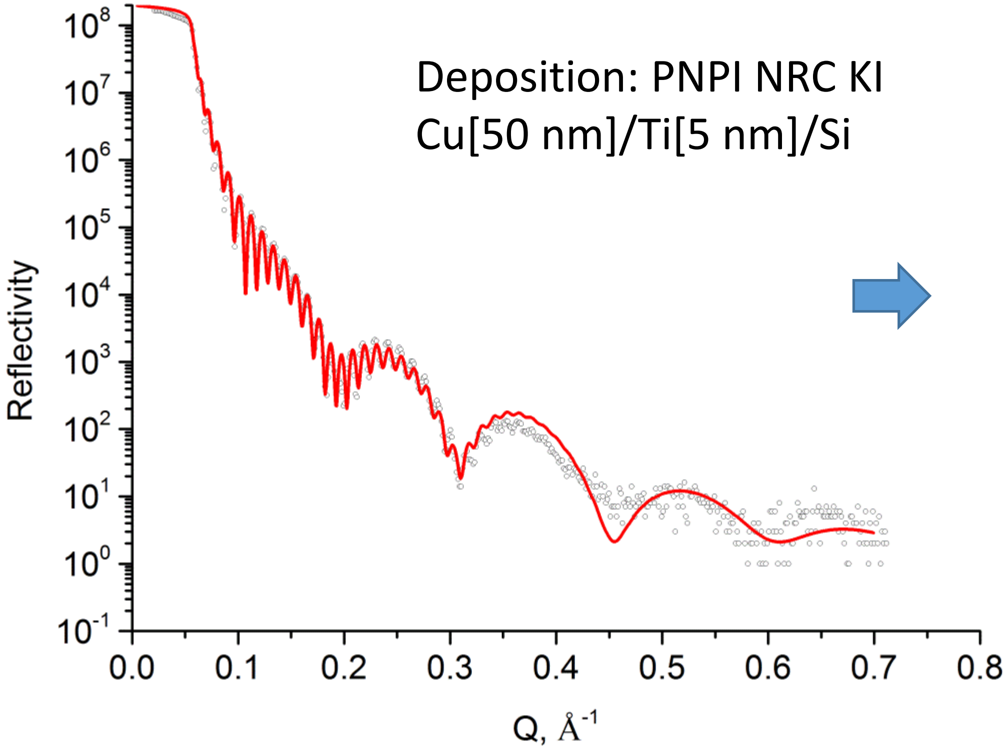


Best material with respect to condition 'electrode SLD = electrolyte SLD'

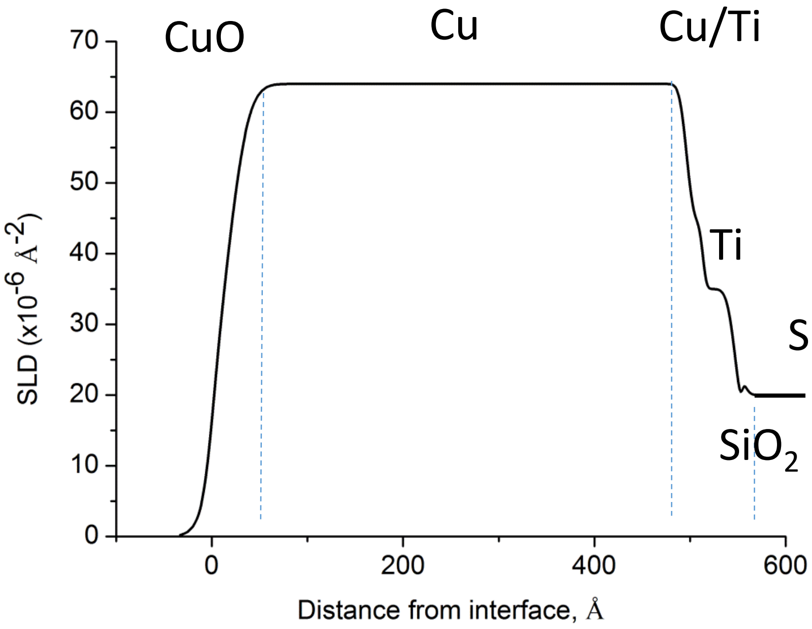
Maximal effect for ~50 nm thick layer

Poor adhesion: additional adhesive layer (Ti, ~5 nm) is required

Deposition and XRR characterization



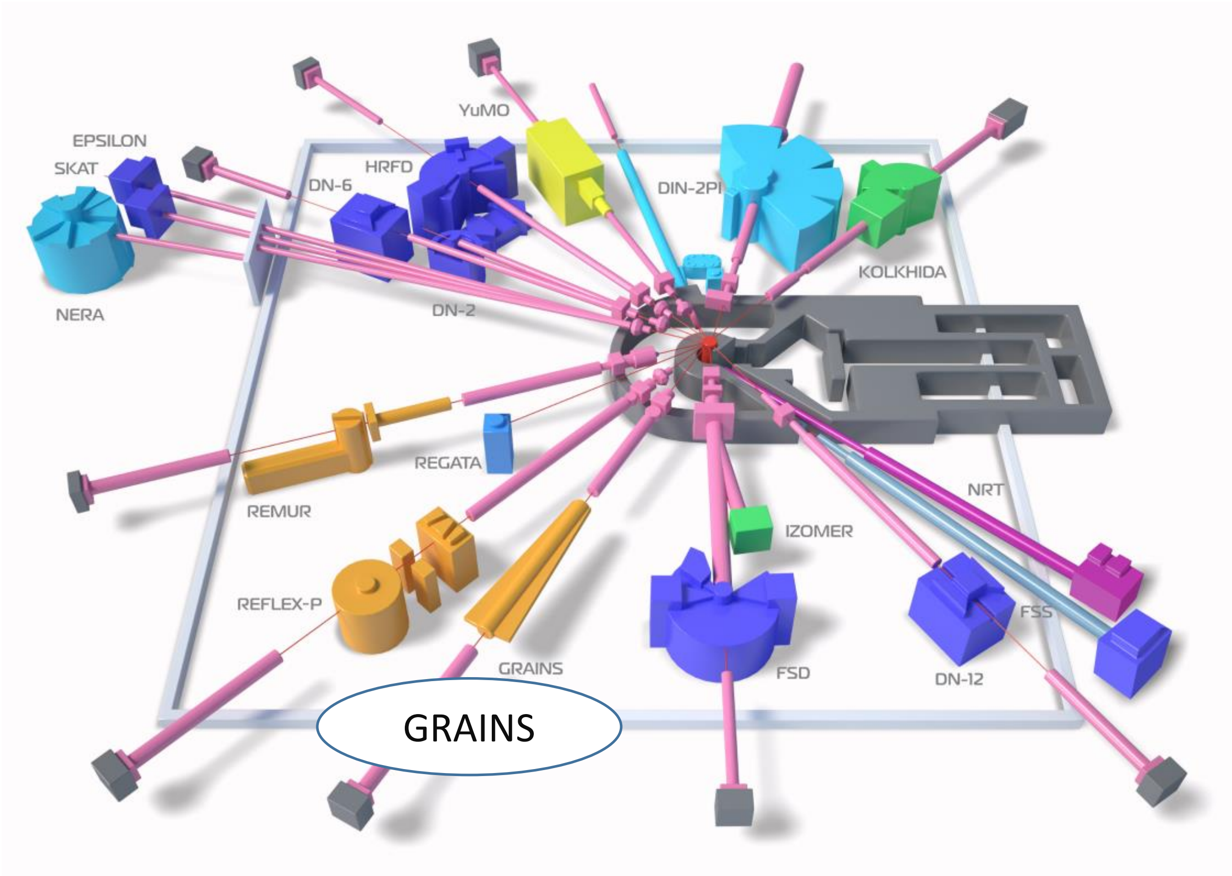
Deposition: PNPI NRC KI
Cu[50 nm]/Ti[5 nm]/Si



Layer	Thickness, Å	SLD, × 10^{-6} Å^{-2}	Roughness, Å
Cu	480	64.3	20
Ti	51	35.0	10
SiO_2	7	15.0	7
Si	-	20.1	2

X-ray measurements:
Centre for X-ray Diffraction Studies, St.-Petersburg State University
http://researchpark.spbu.ru/en/xrd-eng

IBR-2 Neutron Scattering Instruments



GRAINS

Diffractometers:

HRFD, RTD, DN-12, DN-6, FSD, SKAT/Epsilon, FSS

Reflectometers:

REMUR, REFLEX, GRAINS

Small-Angle Scattering:

YuMO

Inelastic Neutron Scattering:

NERA-PR, DIN-2PI

Neutron Imaging:

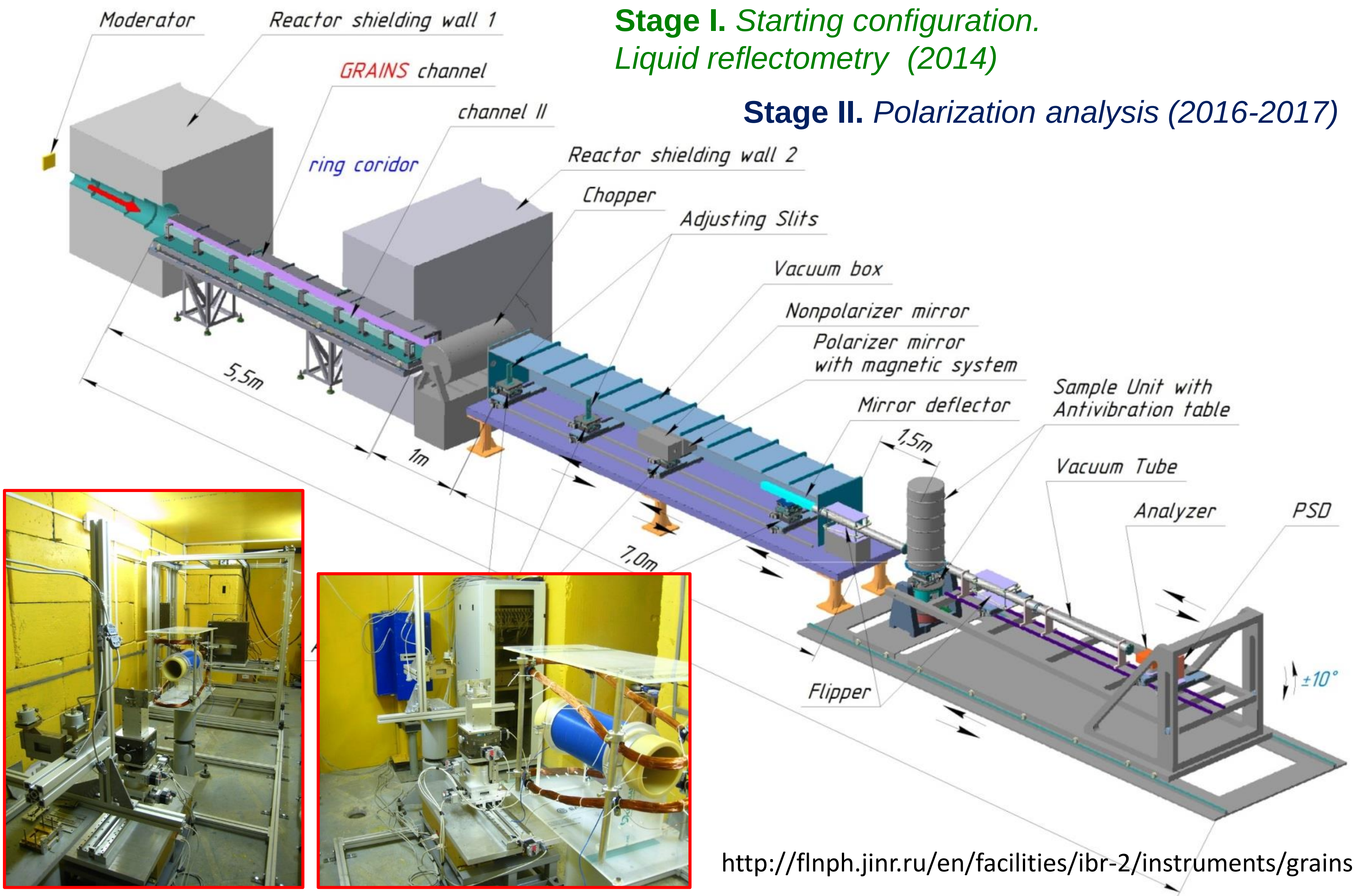
NRT

http://ibr-2.jinr.ru – User Policy

Multifunctional neutron reflectometer GRAINS with a horizontal sample plane at the pulsed IBR-2 reactor (JINR, Dubna)

Stage I. *Starting configuration.*
Liquid reflectometry (2014)

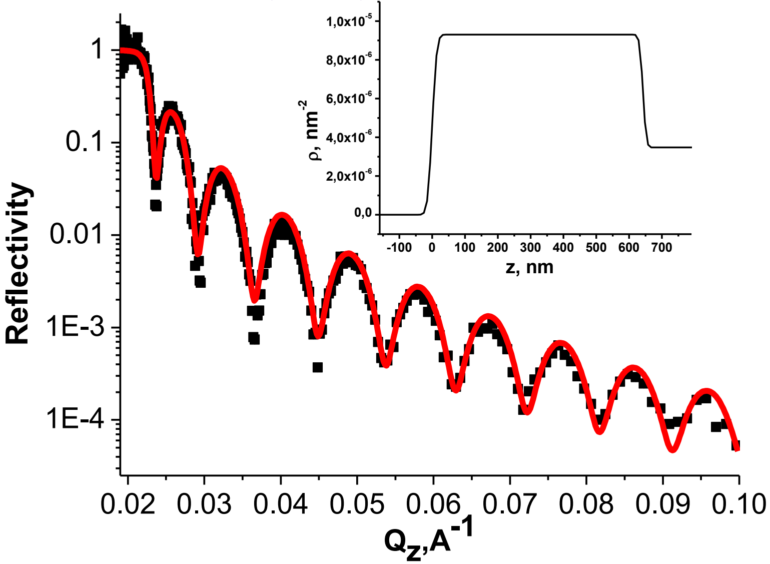
Stage II. *Polarization analysis (2016-2017)*



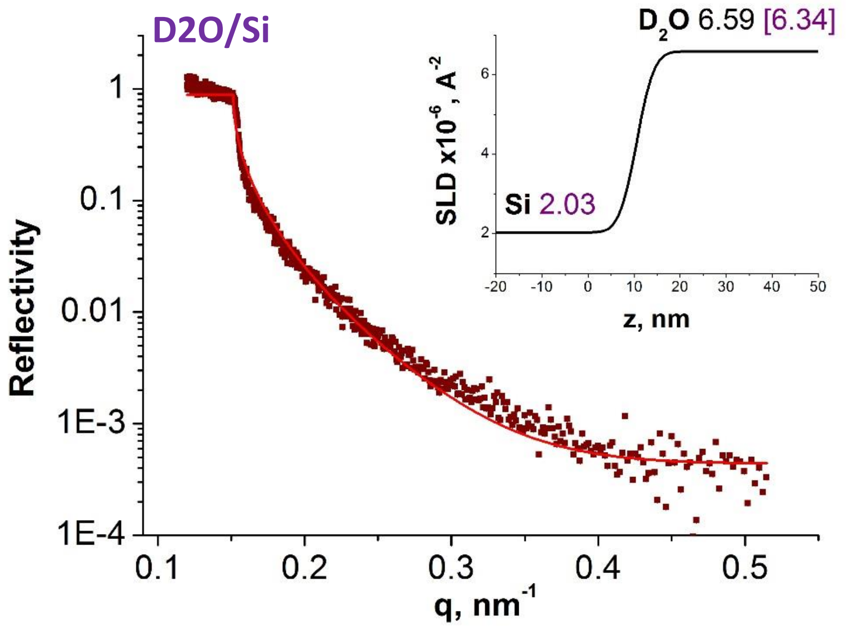
http://flnph.jinr.ru/en/facilities/ibr-2/instruments/grains

NR measurements at air/solid, air/liquid and solid/liquid interfaces

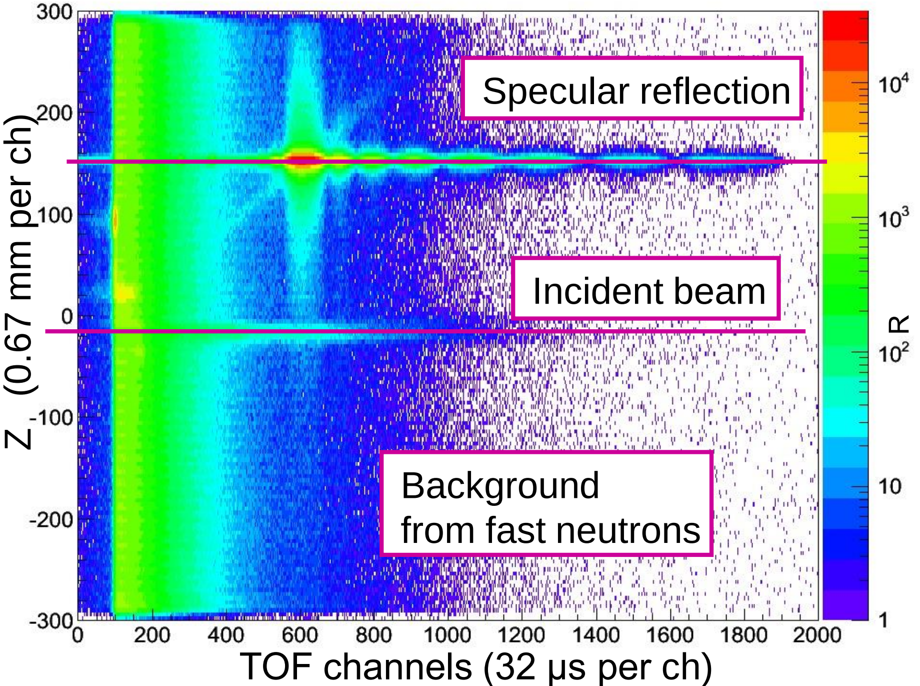
NiMo(650A)/Si (PNPI NRC KI)



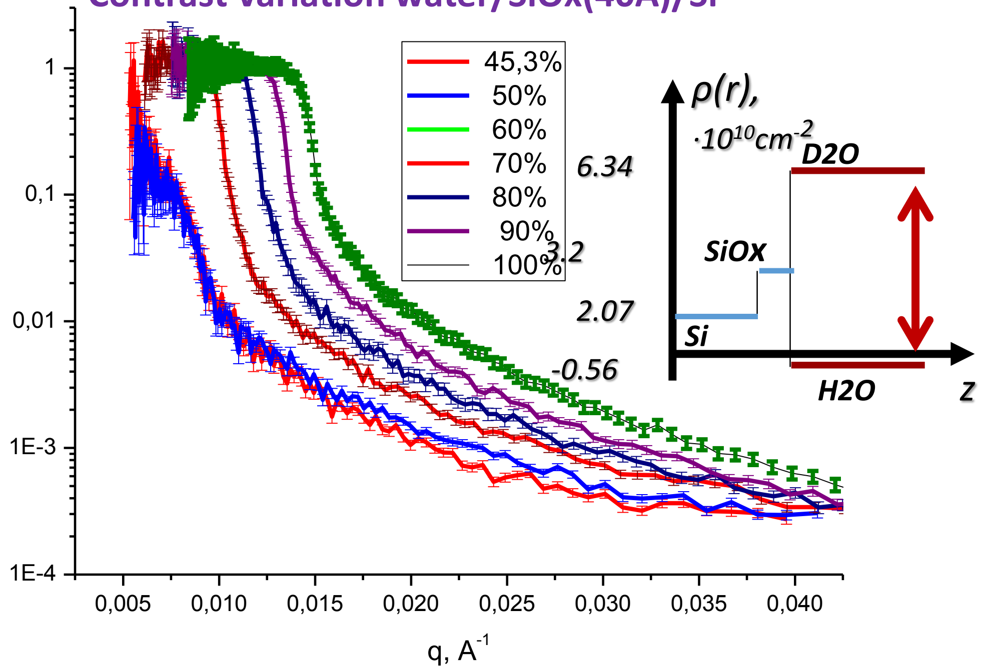
D2O/Si



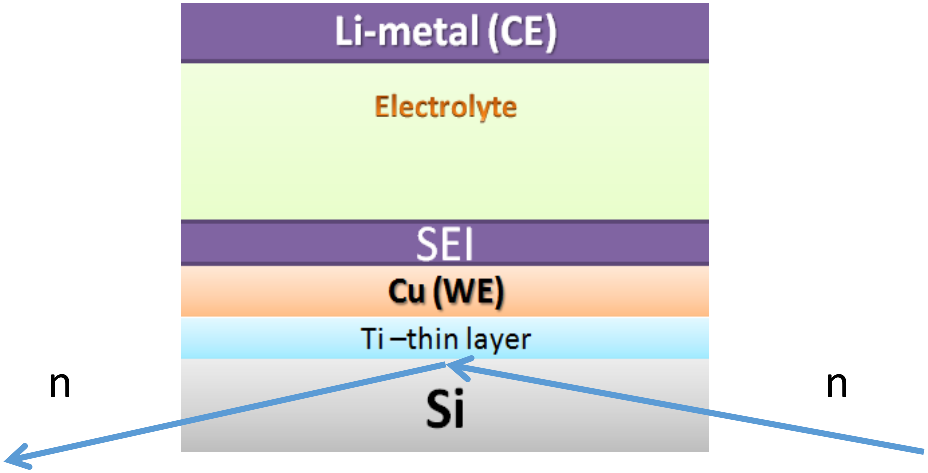
Ni(8.4nm)Ti(7nm)x8/Floatglass (MIRROTRON Ltd.)

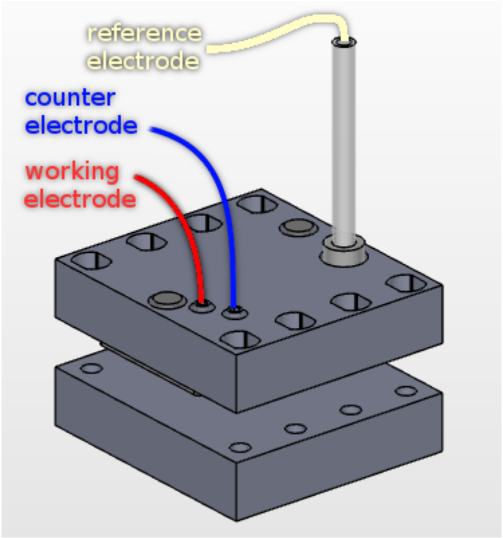


Contrast variation water/SiOx(40A)/Si

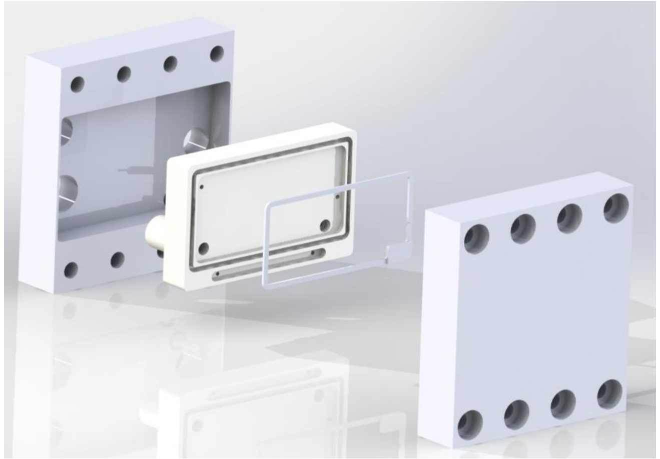


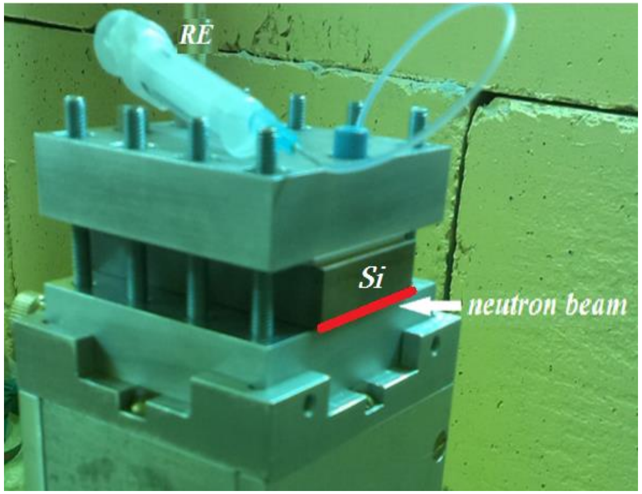
Electrochemical cell for *in operando* NR measurements



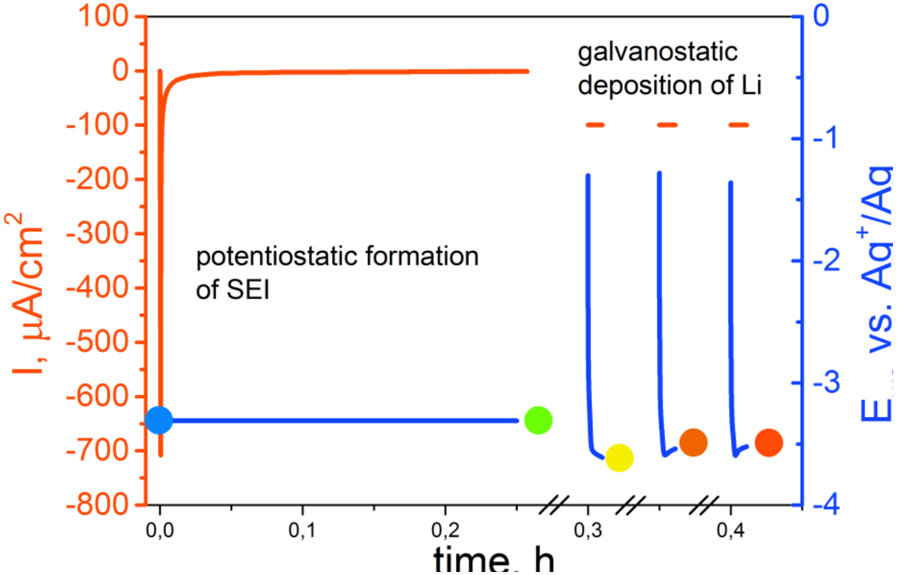


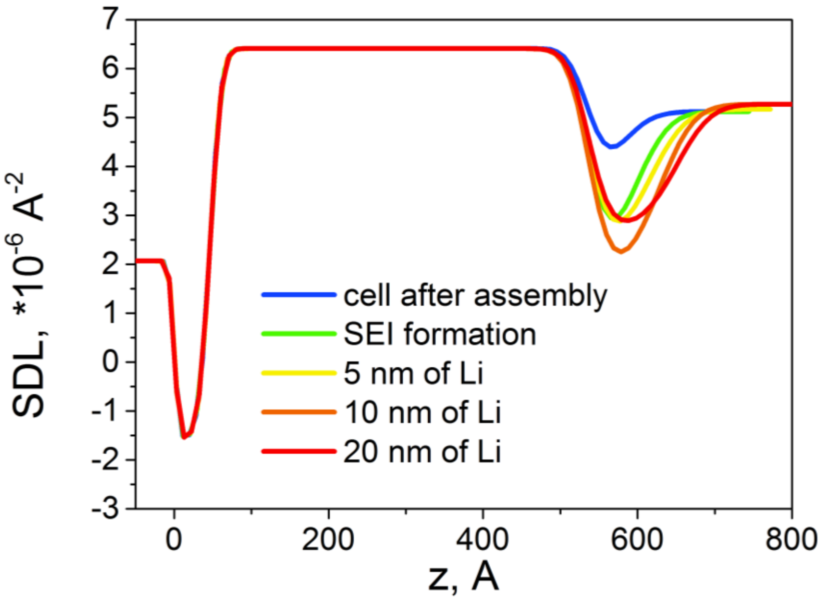
Configuration of originally designed three electrode electrochemical cell for in operando neutron reflectometry

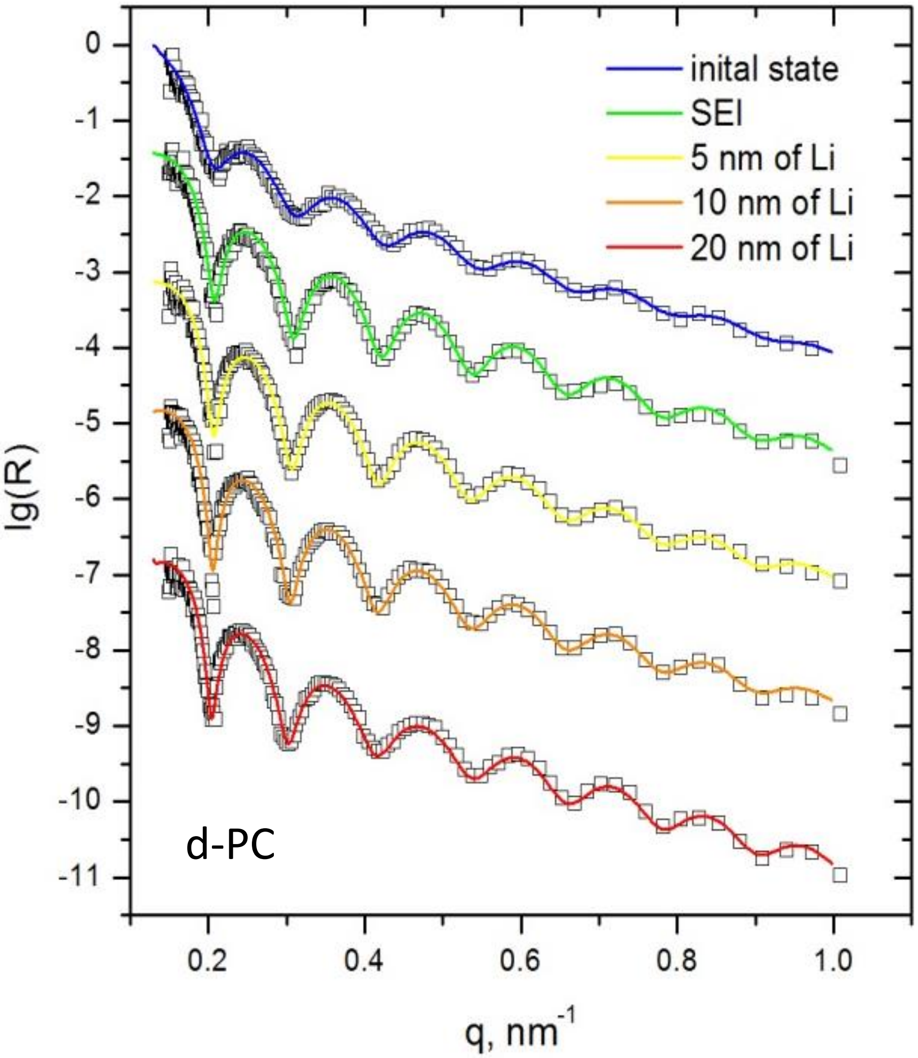




Neutron reflectivity experiments



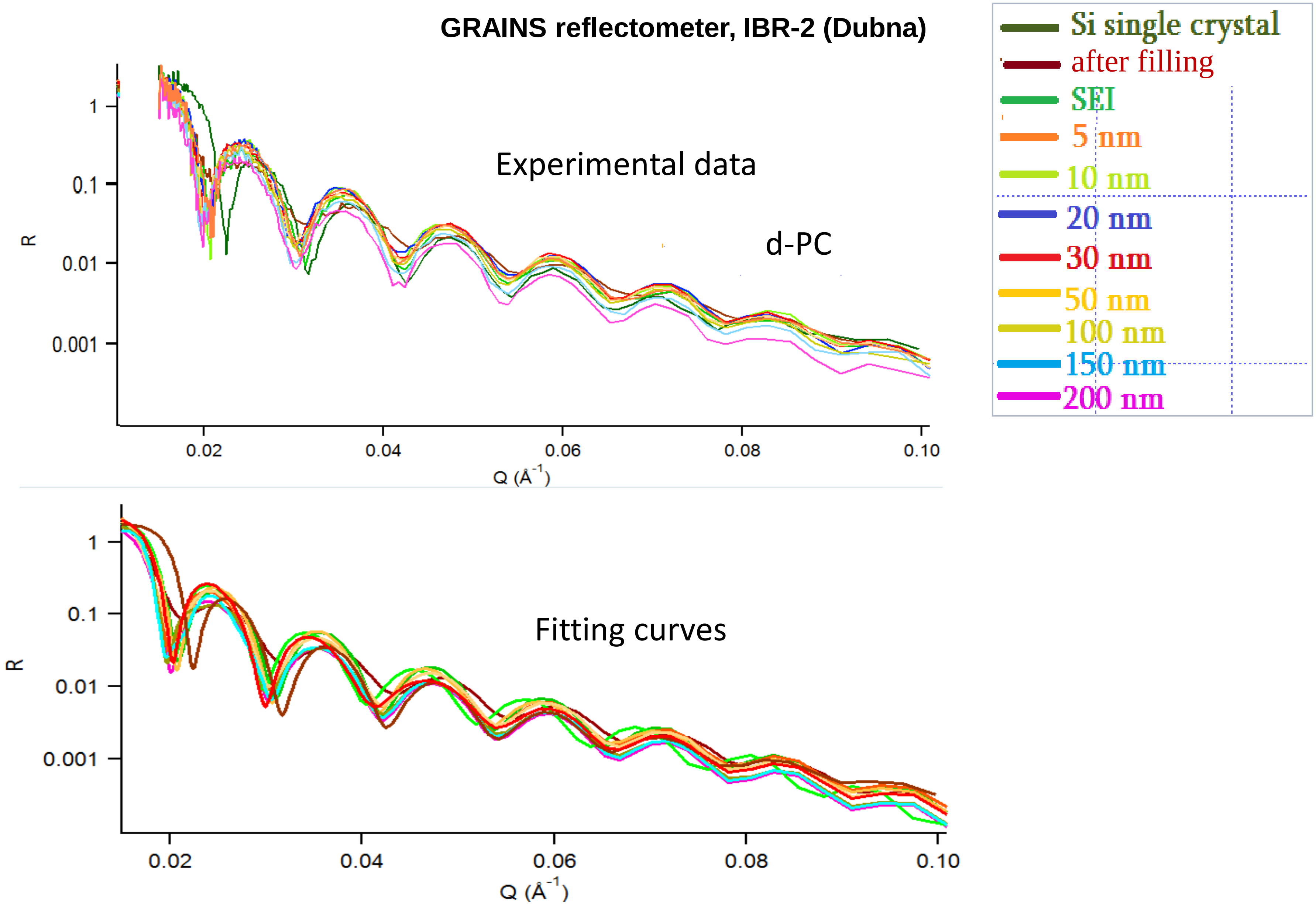




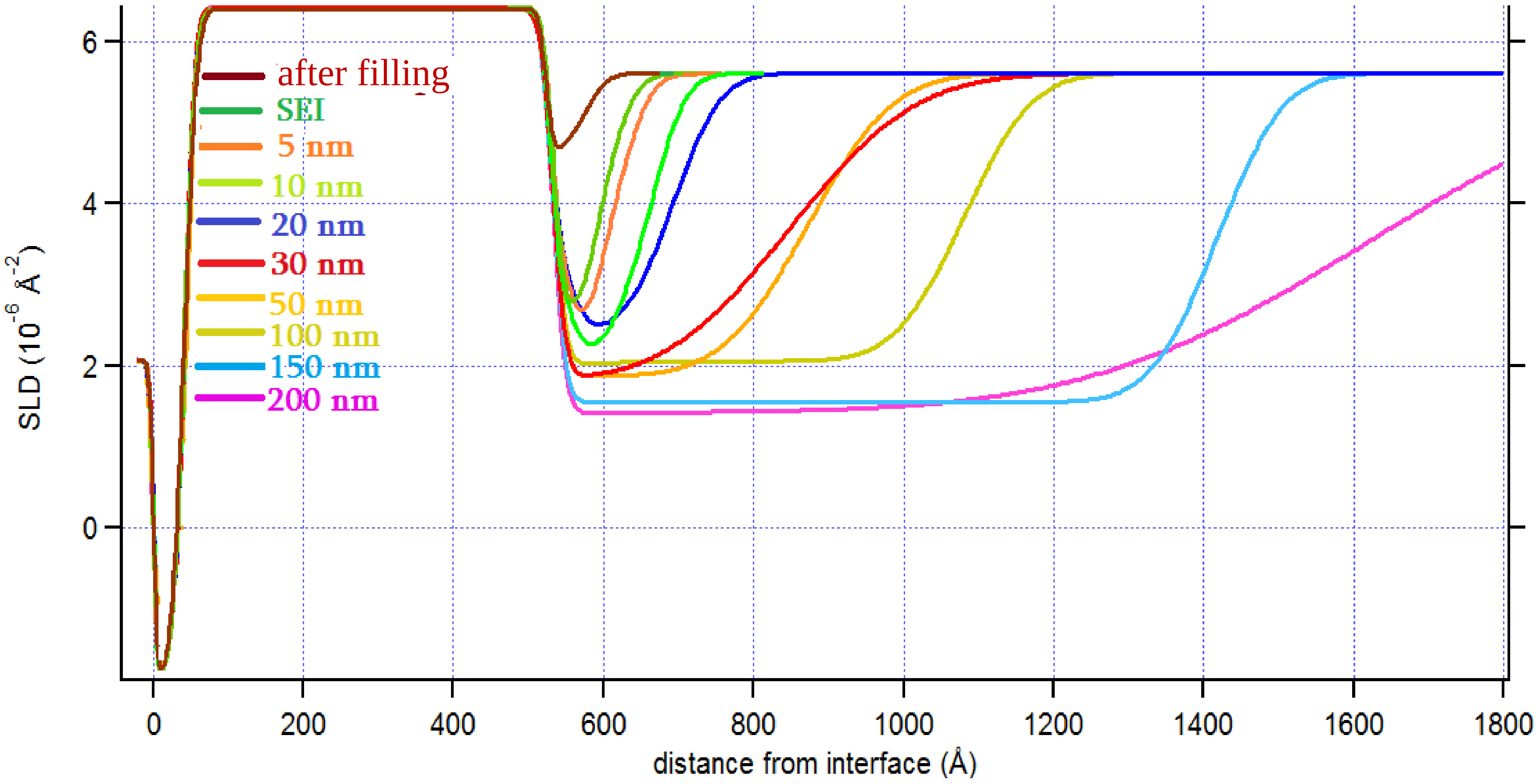
V.I.Bodnarchuk, A.A.Rulev, E.E.Ushakova, M.V.Avdeev, V.I.Petrenko, et al., Submitted to Appl. Surf. Sci.

Neutron reflectivity experiments

GRAINS reflectometer, IBR-2 (Dubna)



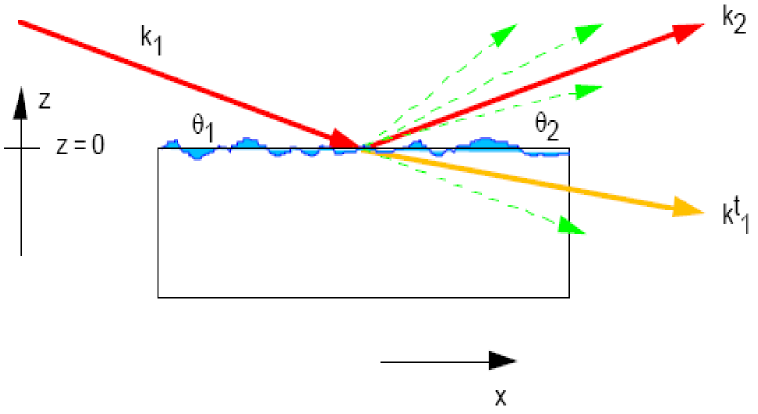
Neutron reflectivity experiments



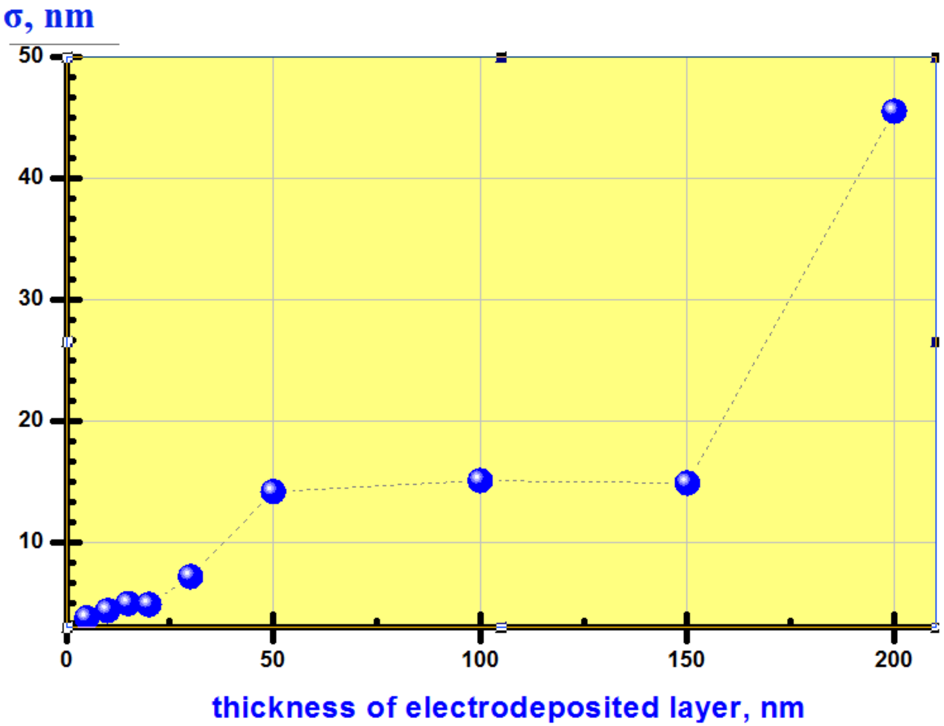
The real-space profile of the scattering length density (SLD) as a function of depth for the electrodeposited layers, showing the evolution of the thickness, SLD, and interface roughness with charge growing. Fits were obtained with several parameters kept constant at values determined from previous OCV simultaneous fit.

Neutron reflectivity experiments

Reflection from Rough Surfaces



$$R = R_F e^{-2k_{1z}k^t_{1z}\sigma^2}$$



Increase in the degree of heterogeneity of the electrodeposited layer (fitting parameter) as a function of rate of the layer thickness (defined as charge passed through the cell).

Conclusions

In contrast to other techniques probing electrochemical interfaces, SANS and NR provide averaged information of the surface layer evolution; this allows one to avoid artefacts related with the locality of information which can be distorted by many factors.

The results of SANS and NR experiments on electrochemical interfaces are indicative of the fact that nanoscale can be important for the microscopic properties of these systems.

Acknowledgments

Russian Ministry of Science and Education project

SYNESTESia

synchrotron and neutron studies for energy storage