Neutron and X-Ray reflectometry studies of planar interfaces for power sources

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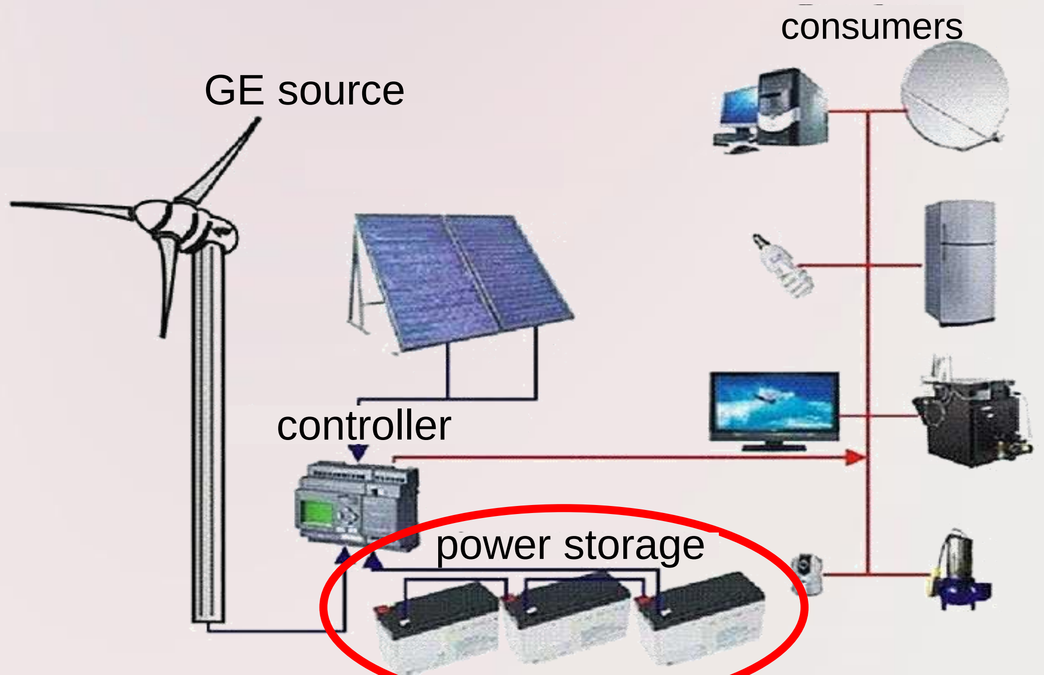
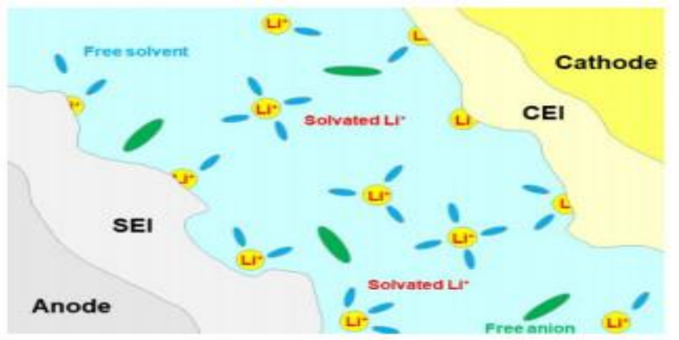
Dubna, 2022

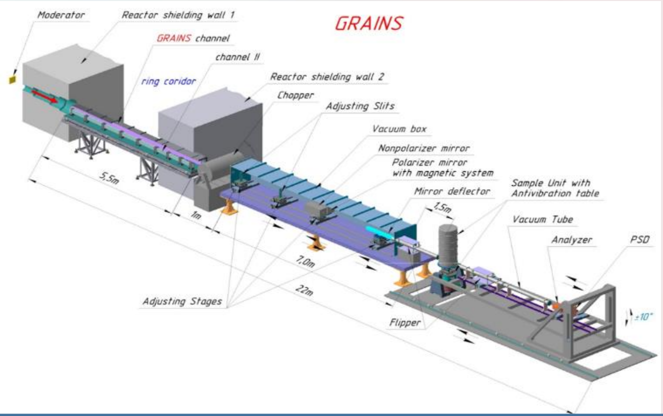
▶ Motivation



Need for development and modernization of existing power sources.

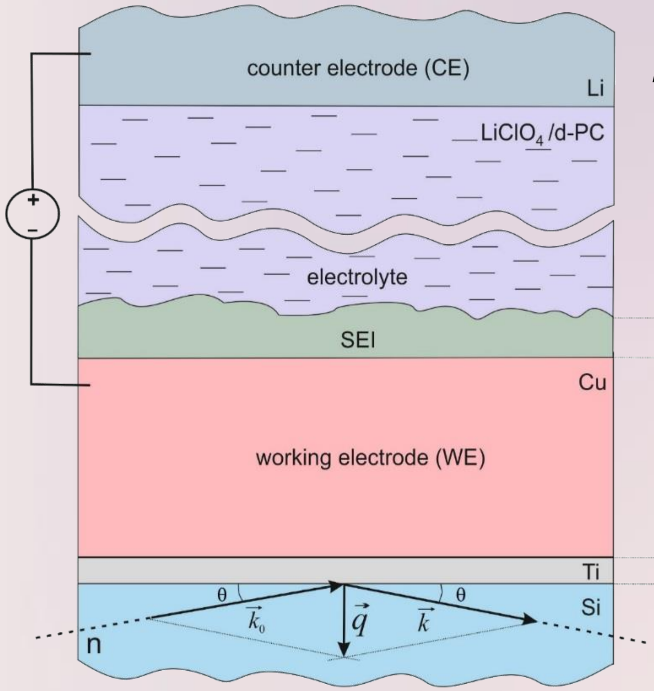
Main parameters:
- Specific capacity (capacity↑ weight/volume↓);
- Life time (number of full cycles);
- Safety;
- Charge time.



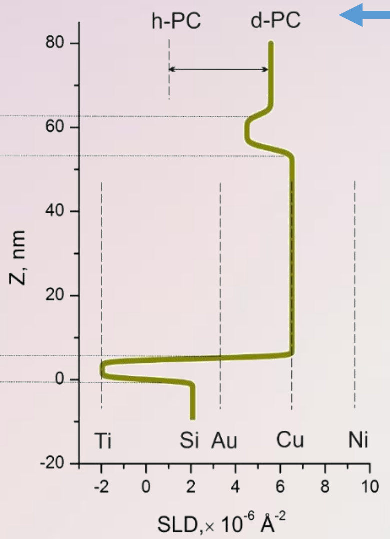


- Buried interfaces under working conditions (in situ/operando);
- Contrast variation

Neutron Reflectometry: Design of experiment and problems

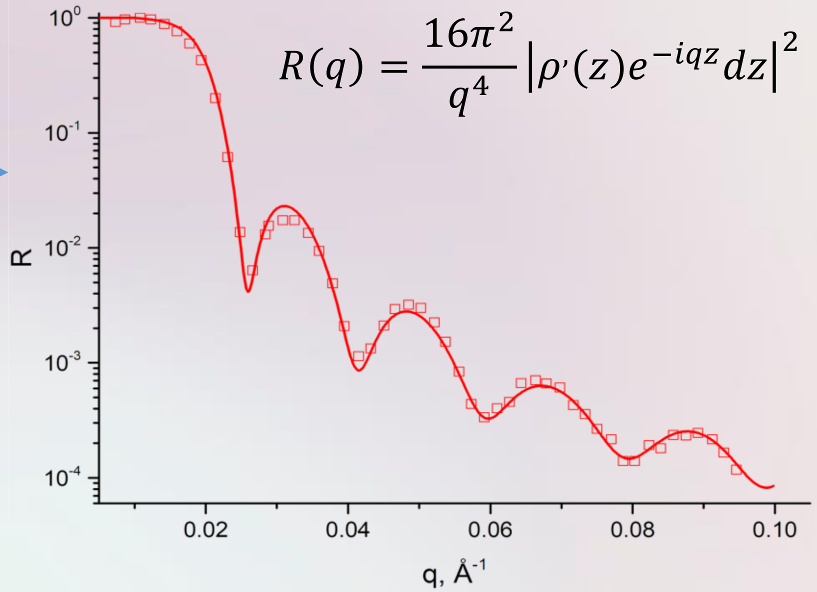


$\rho(z)$ – SLD (*scattering length density*) distribution profile in depth of the sample



Fourier transform

$$R(q) = \frac{16\pi^2}{q^4}\left|\rho'(z)e^{-iqz}dz\right|^2$$



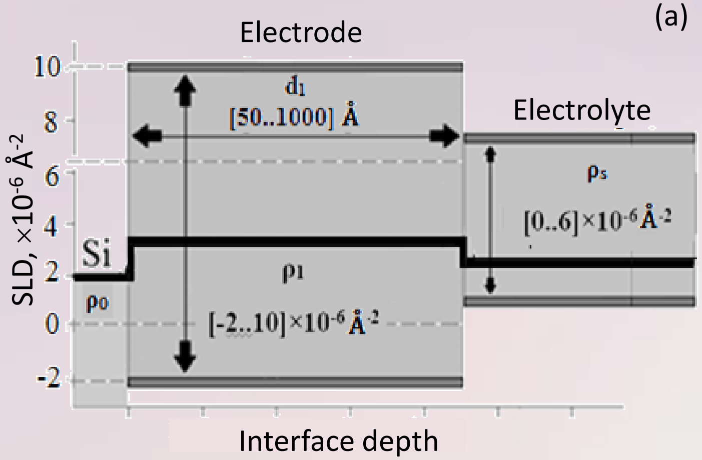
Li-ion batteries with metal anodes and liquid electrolytes

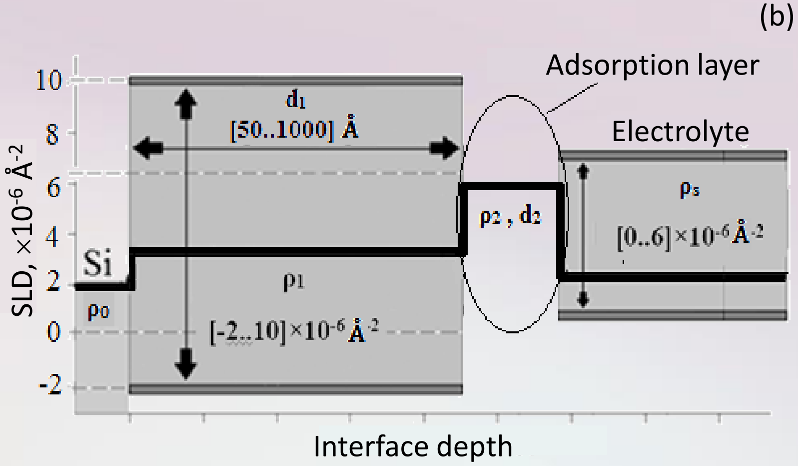
Problems:

- Optimization of design of experiment to increase NR sensitivity regarding detection of SEI and Li deposition layer;
- Development of experimental cells for NR experiments with liquid electrolytes;
- Study of SEI formation and evolution of electrochemical interfaces during battery operation;
- Modification of electrolytes to prevent non-uniform Li deposition.

▶ Optimization of the initial interface structure

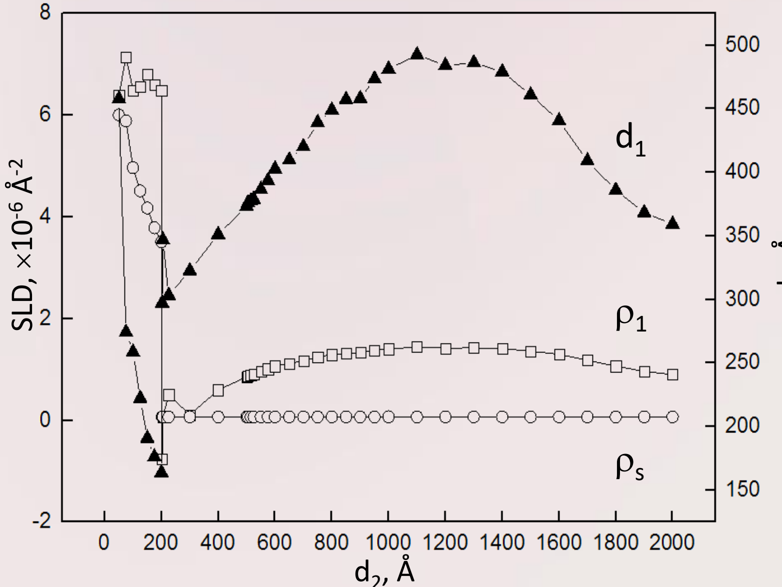
Optimization of initial interface structure



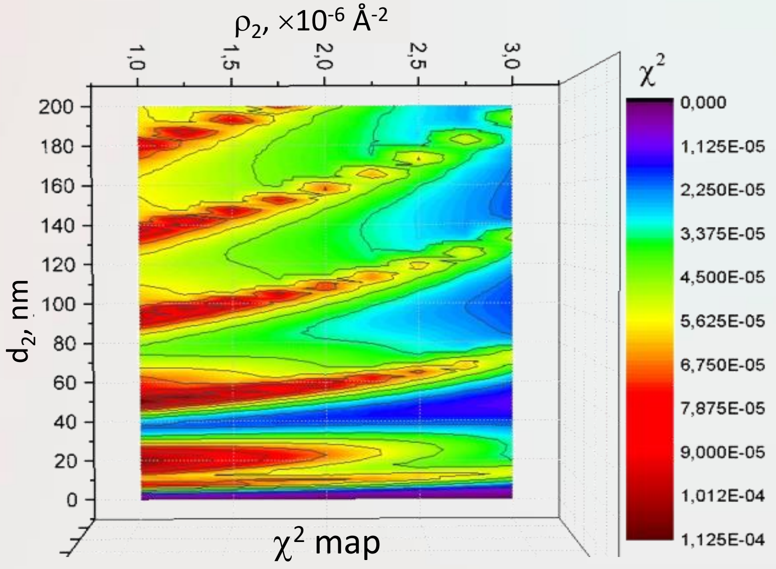


Maximization of $\chi^2 = \frac{\int dq_z[R_2(q_z,\rho_0,\rho_1,\rho_2,\rho_s,d_1,d_2)-R_1(q_z,\rho_0,\rho_1,\rho_s,d_1)]^2}{\int dq_z[R_1(q_z,\rho_0,\rho_1,\rho_s,d_1)+B]^2}$

Optimal values



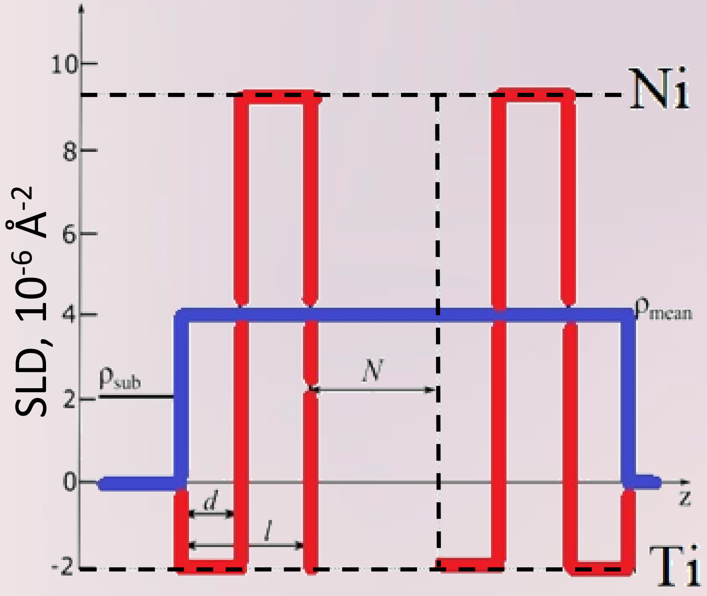
ρ_2 release ⟷



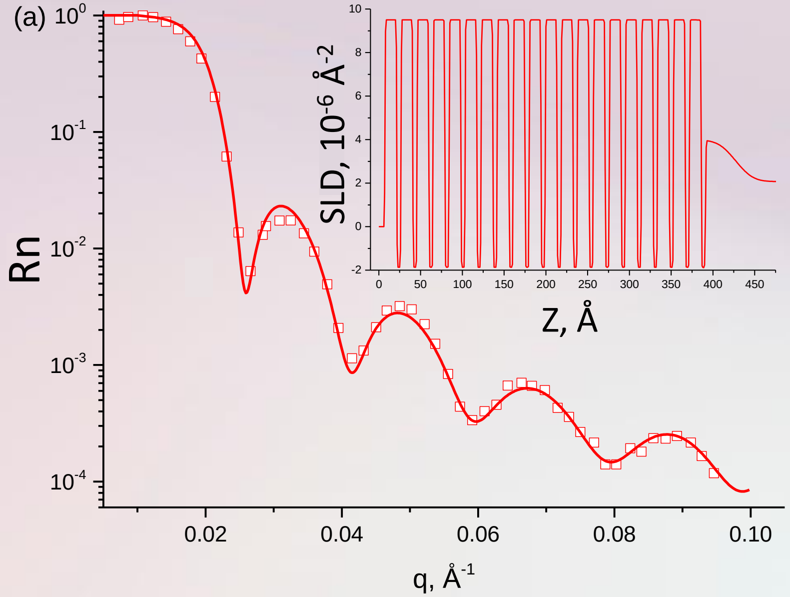
Thin adsorption layer (up to 200 Å):
- Electrode SLD ≈ 6 * 10^{-6}Å^{-2} (Cu);
- Electrode thickness ≈ 450 Å;
- Deuterated electrolyte.

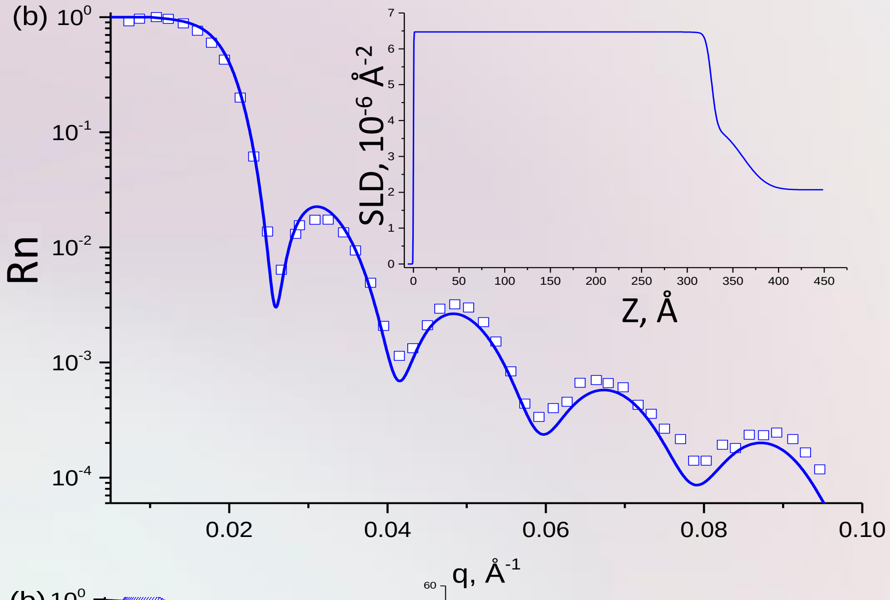
Thick adsorption layer (over 200 Å):
- Electrode SLD ≈ 1 * 10^{-6}Å^{-2} (Li, Na, **???**);
- Electrode thickness ≈ 450 Å;
- Protonated electrolyte.

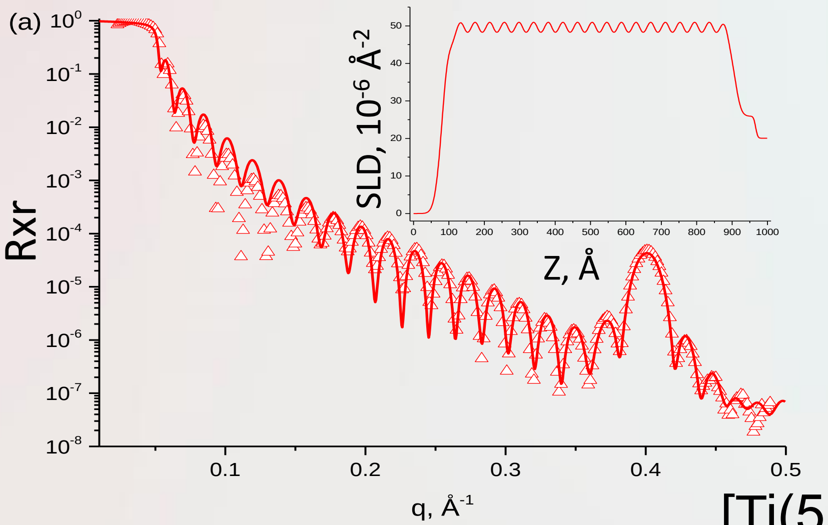
► *Quasimonolayer approximation (usage for all types of NR samples)*

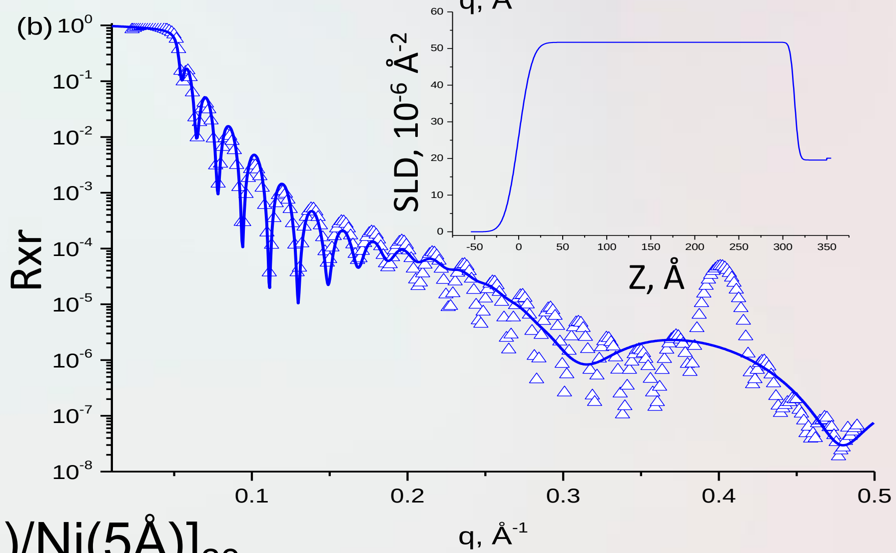


$$\rho_m = (d/l)\rho_1 + (1 - d/l)\rho_2$$





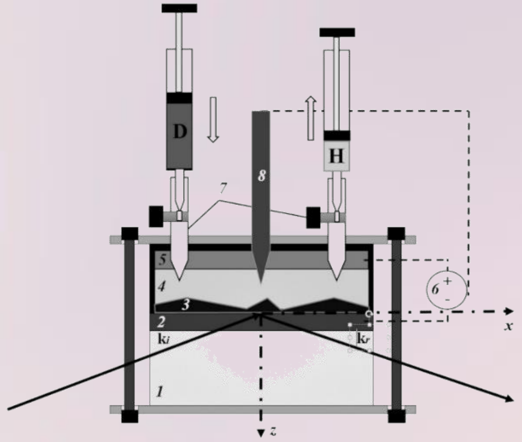


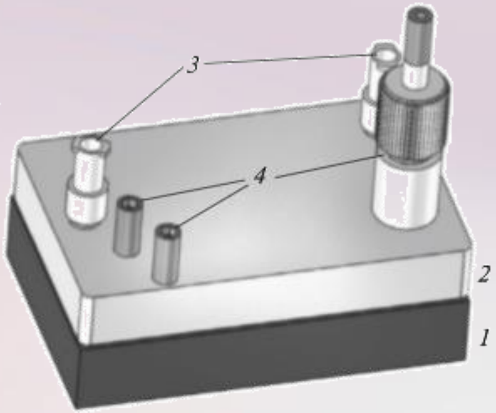


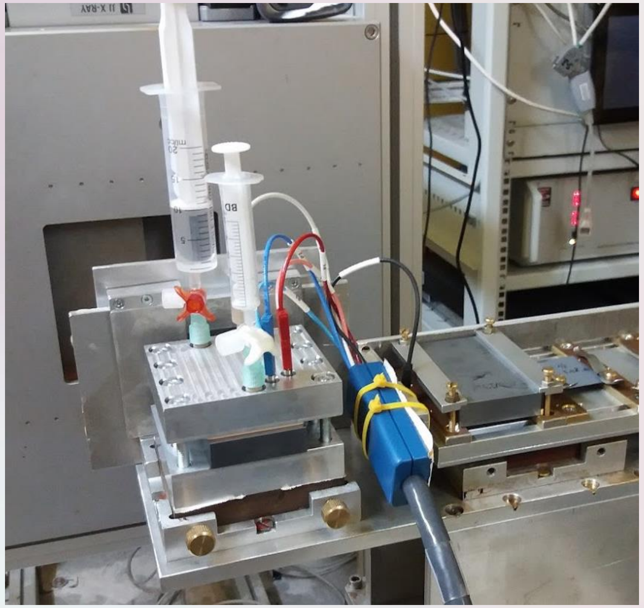
$[Ti(5Å)/Ni(5Å)]_{20}$

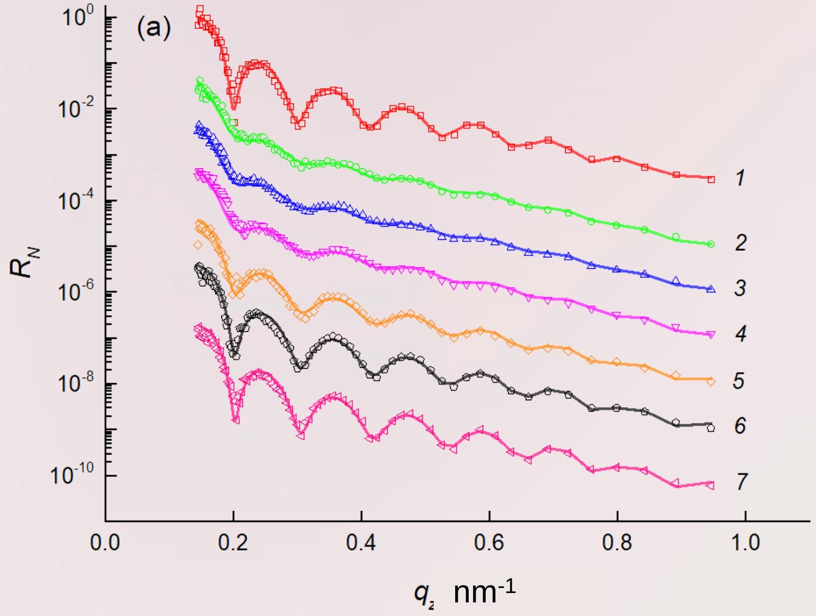
Ye.Kosiachkin et.al. *Low-period Ni/Ti multilayers with varied quasi-homogeneous structure for neutron reflectometry for electrochemical interfaces.* Thin Solid Films (**submitted**)

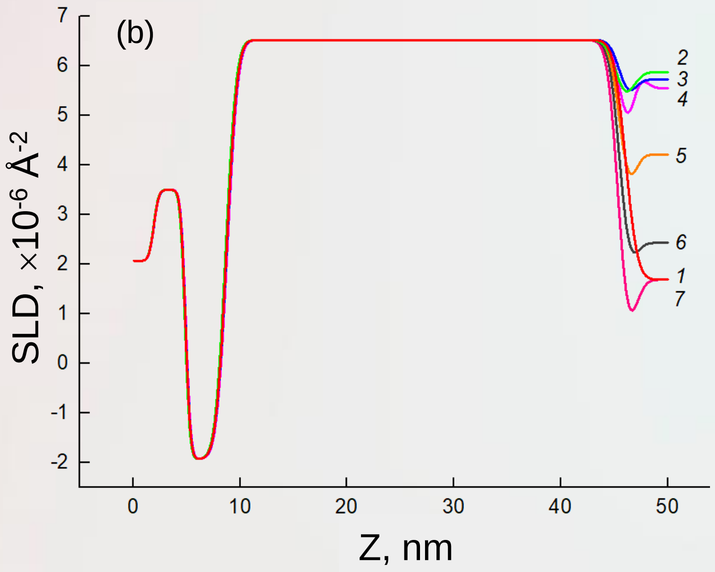
▶ Cell for electrochemical experiments with liquid electrolytes











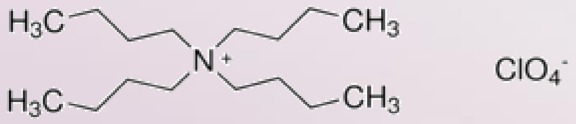
0.5 M $LiClO_4$ in 1:1 EC:DMC

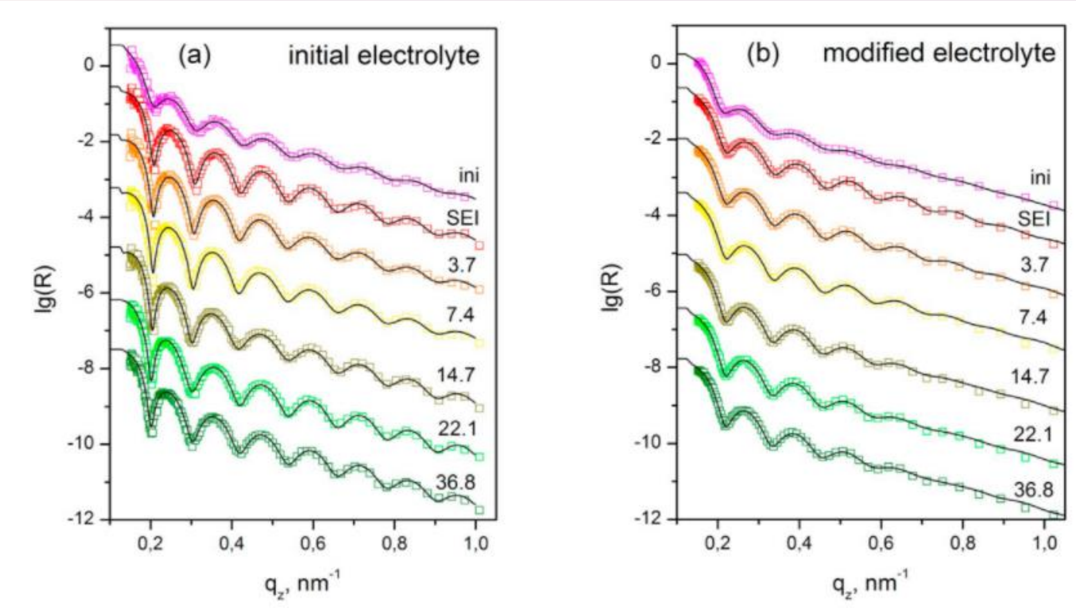
SEI ≈ 10 Å, non-uniform

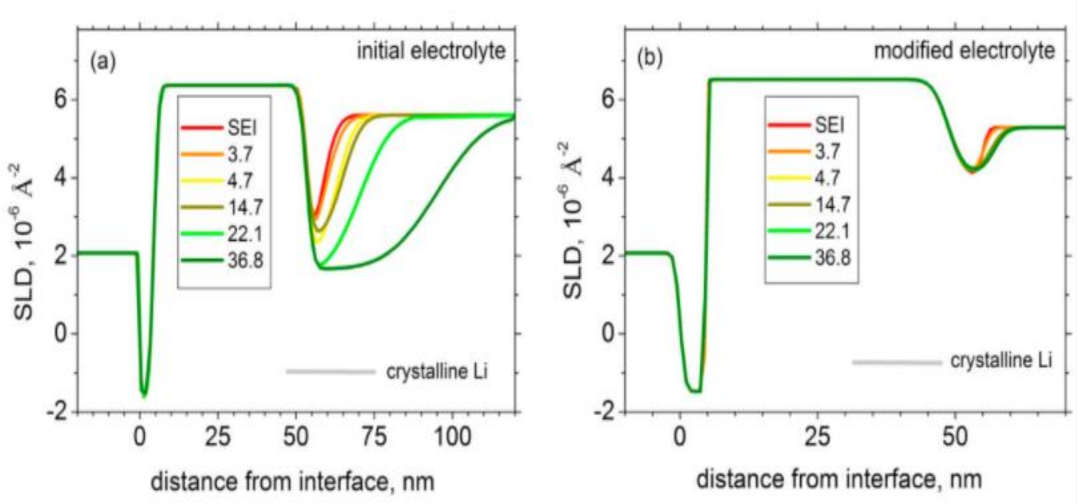
SEIs liquid phase SLD grows proportional with contrast variation

Kosiachkin, Y.N., *et al.* Structural Studies of Electrochemical Interfaces with Liquid Electrolytes Using Neutron Reflectometry: Experimental Aspects. *J. Surf. Investig.* 15, 787–792 (2021). https://doi.org/10.1134/S1027451021040285

▶ Liquid electrolyte modification with TBAP







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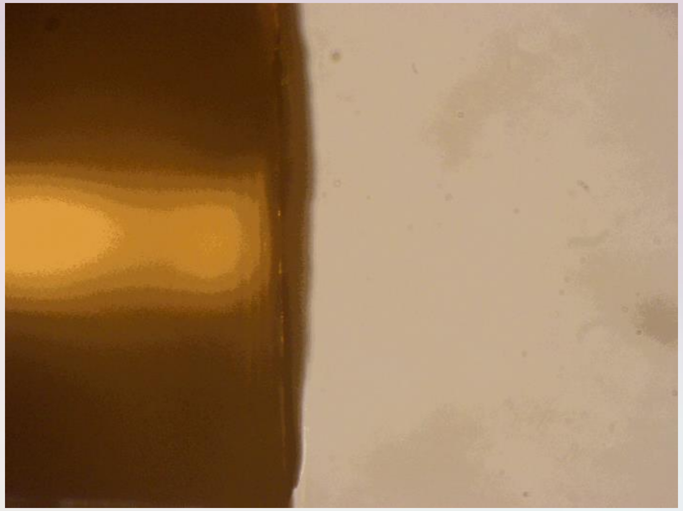
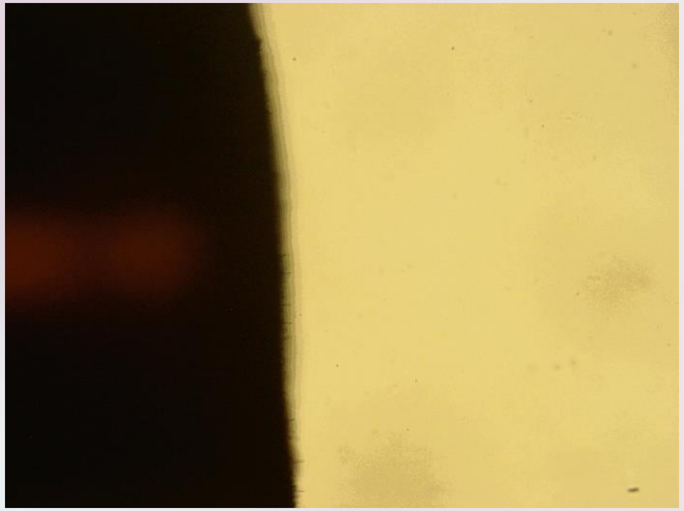
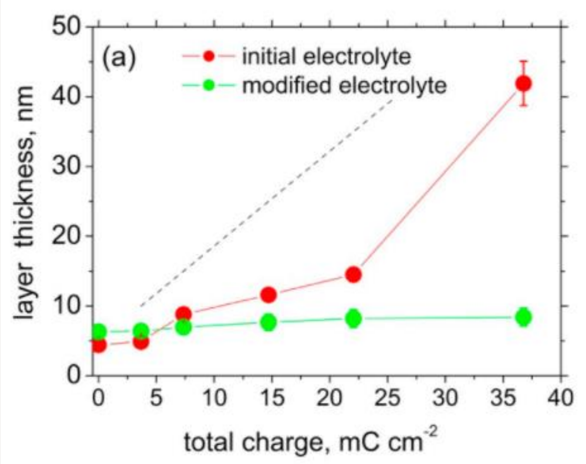


Li electrode, 0.1M $LiClO_4$ in **PC**, i = 5 μA cm^{-2}



Li electrode, 0.1M $LiClO_4$ in **PC** + 1 M **TBAP**, i = 5 μA cm^{-2}



Strong suppression of Li migration

↓

Capacity loss!

Avdeev, M. V., Rulev, A. A., Ushakova, E. E., Kosiachkin, Y. N., Petrenko, V. I., Gapon, I. V., ... & Itkis, D. M. On nanoscale structure of planar electrochemical interfaces metal/liquid lithium ion electrolyte by neutron reflectometry. *Applied Surface Science*, *486*, 287-291, (2019).

Conclusions

To study processes, that affect on the main batteries properties next works were done:

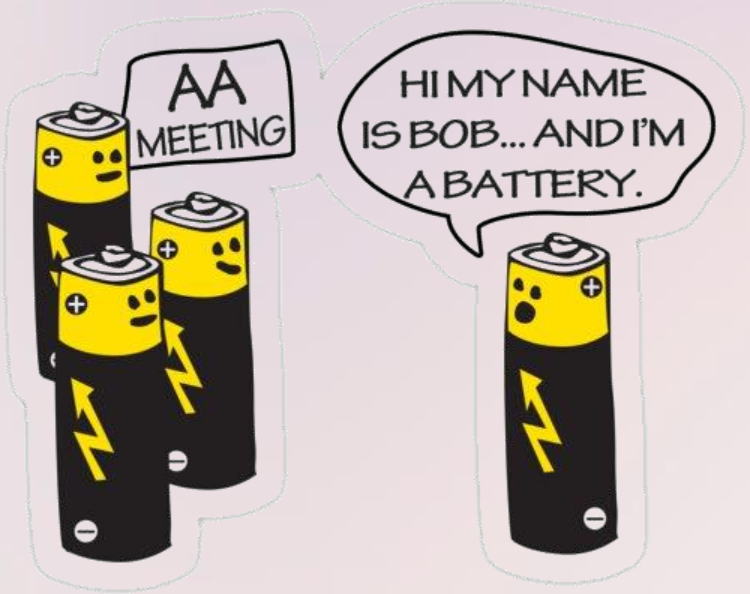
- Regulation of sensitivity of NR is studied and can be regulated and enhanced by varying the scattering contrasts between interface components. Optimal configurations for two regimes of SEI layer thickness (thin < 200 Å, thick > 200 Å) were determined.

- Multilayers were tested for quasi-continuous variation SLD of support layer.

- Specialized cell for NR experiments with liquid electrolytes was developed. The contrast variation experiments based on H/D substitution in liquid electrolyte confirmed ability of the method to detect layers with thickness down to 1 nm;

- Liquid electrolyte was modified with TBAP additives. Strong suppression of Li migration is observed.

►*Thank you for attention!*



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