Skoltech

LOMONOSOV MOSCOW STATE UNIVERSITY

RSF Russian Science Foundation

Crystallography and Crystal Chemistry
VIII International School-Conference of Young Scientists 2023

NMR as a Tool to Study Metal-Ion Battery Electrolytes

Dr. Olga I. Shmatova

PhD in Chemistry, Assistant Professor

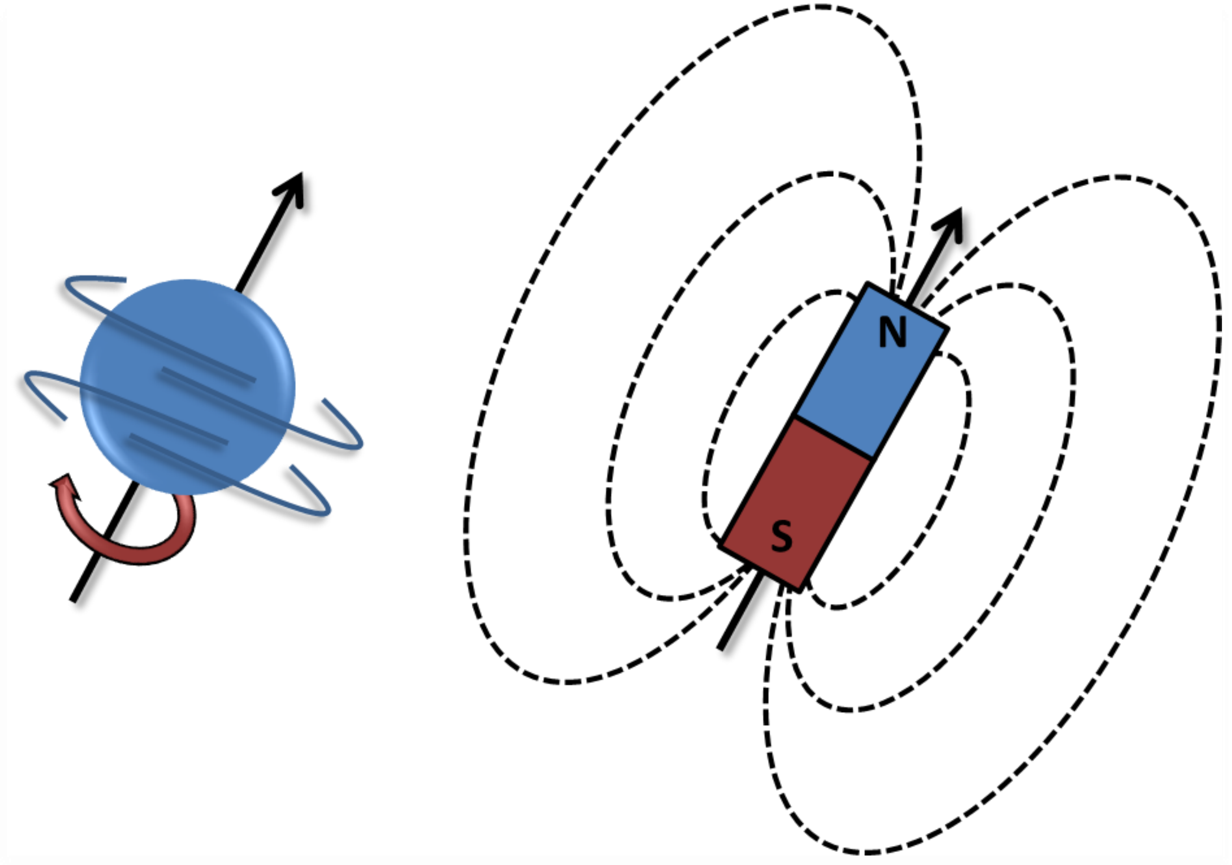
Center for Energy Science and Technology

Skoltech, Moscow, Russian Federation

November 12th, 2023

Magnetic properties of nuclei

Spinning proton creates a magnetic field



Nuclei characteristics:

- **M** – mass;
- **Z** – charger;
- **P** – angular momentum (angular momentum);
- **μ** – magnetic moment;
- **χ** – gyromagnetic ratio;
- **I** – spin quantum number, determines the number of allowed orientations of the μ nucleus in a constant magnetic field;
- **h** – Planck constant $6.626 \cdot 10^{-34}$ kg*m²/s.

$$P = Ih/2\pi$$

$$\mu = \gamma P = \gamma I h/2\pi$$

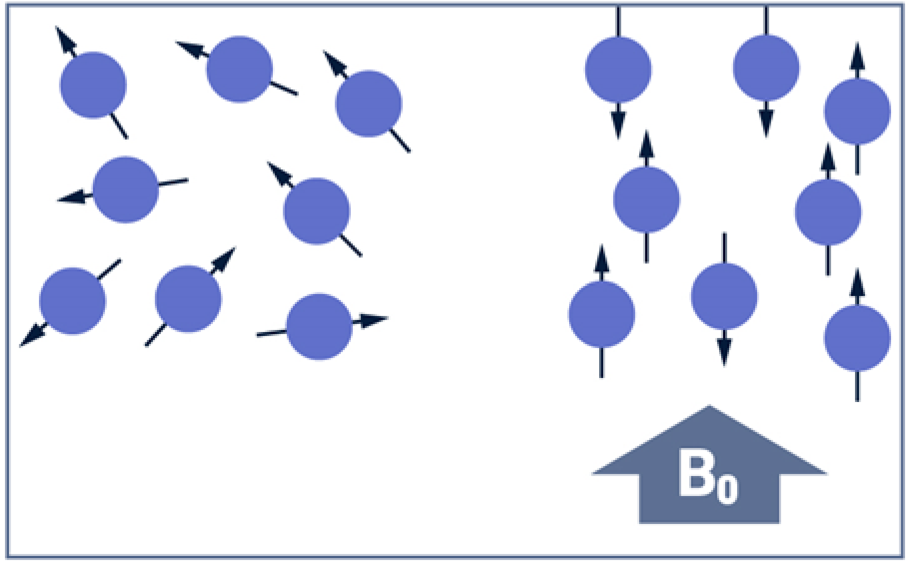
This work is funded by Russian Science Foundation (grant №23-23-00343).

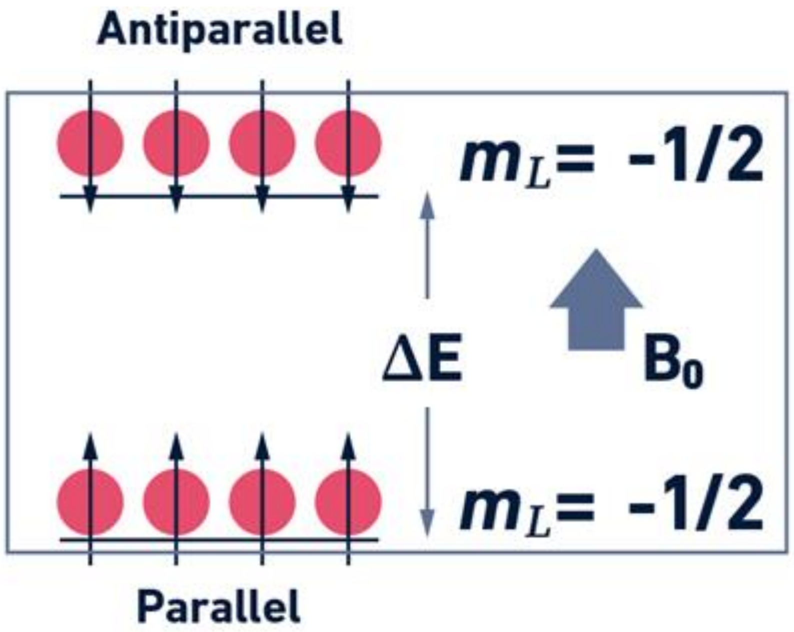
Nuclear magnetic resonance. Zeeman effect

$\mu = \gamma P = \gamma I h/2\pi$

μ – magnetic moment;
I – spin quantum number,
γ – gyromagnetic ratio,
P – angular momentum (moment of momentum or rotational momentum)

$I = 1/2$

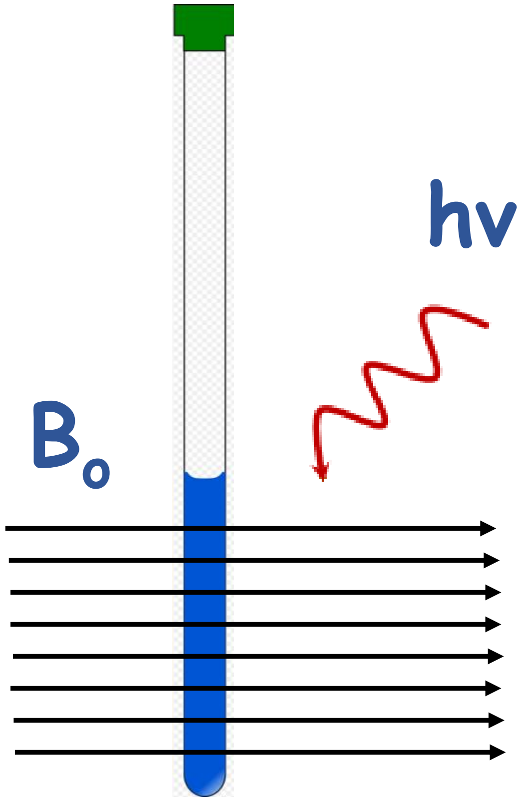




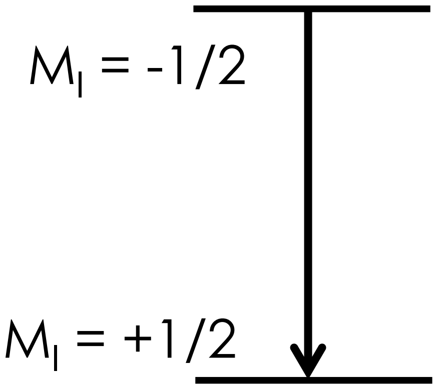
$\Delta E = 2\mu B_0 = h\nu$

This work is funded by Russian Science Foundation (grant №23-23-00343).

Nuclear magnetic resonance



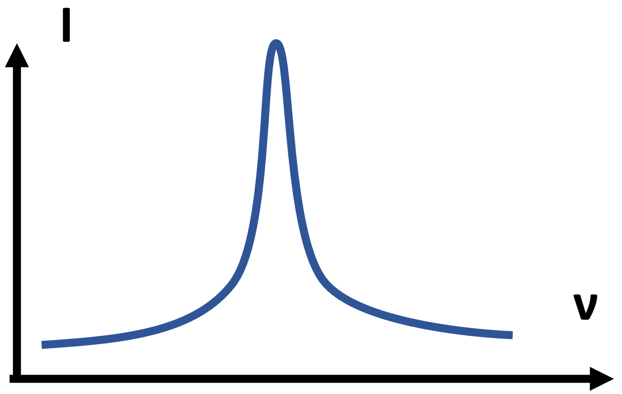
$$\Delta E = 2\mu B_0 = h\nu$$



Relaxation

Seconds or fractions of second

Emission spectrum



I – spin quantum number,
ɣ – gyromagnetic ratio

$$\mu = \gamma P = \gamma I h/2\pi$$

Equilibrium population of energy levels
Boltzmann equation

$$N1/N2 = \exp(-\Delta E/kT) \approx \exp(-\gamma h B_0/2\pi kT)$$

This work is funded by Russian Science Foundation (grant №23-23-00343).

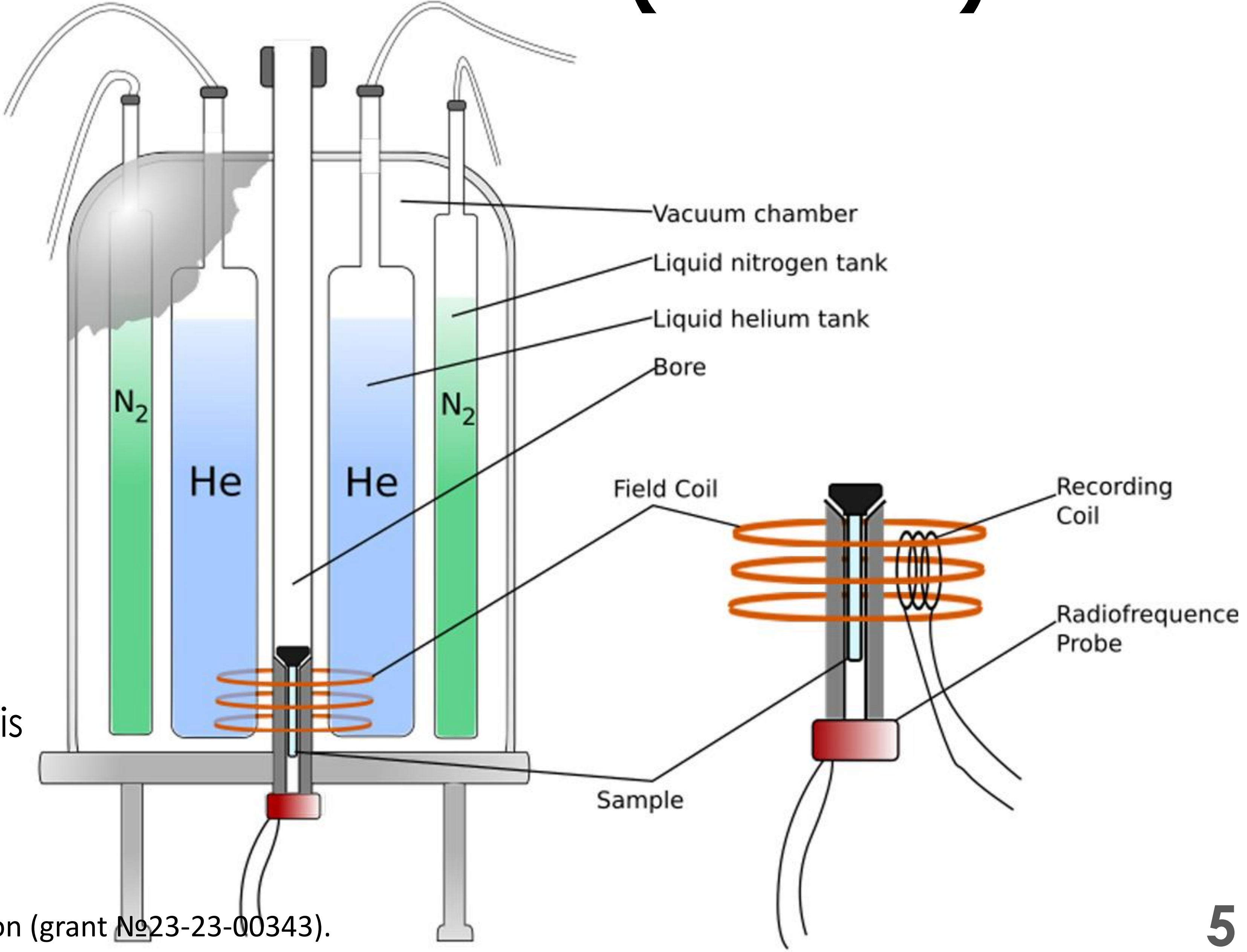
Pulse or Fourier-Transform NMR (FT-NMR)

A strong magnetic field is a must! (provided by a superconducting magnet)

Short high-power RF pulse:
~50 watt, τ =10-50 μs
with a frequency close to ν_0

⇩

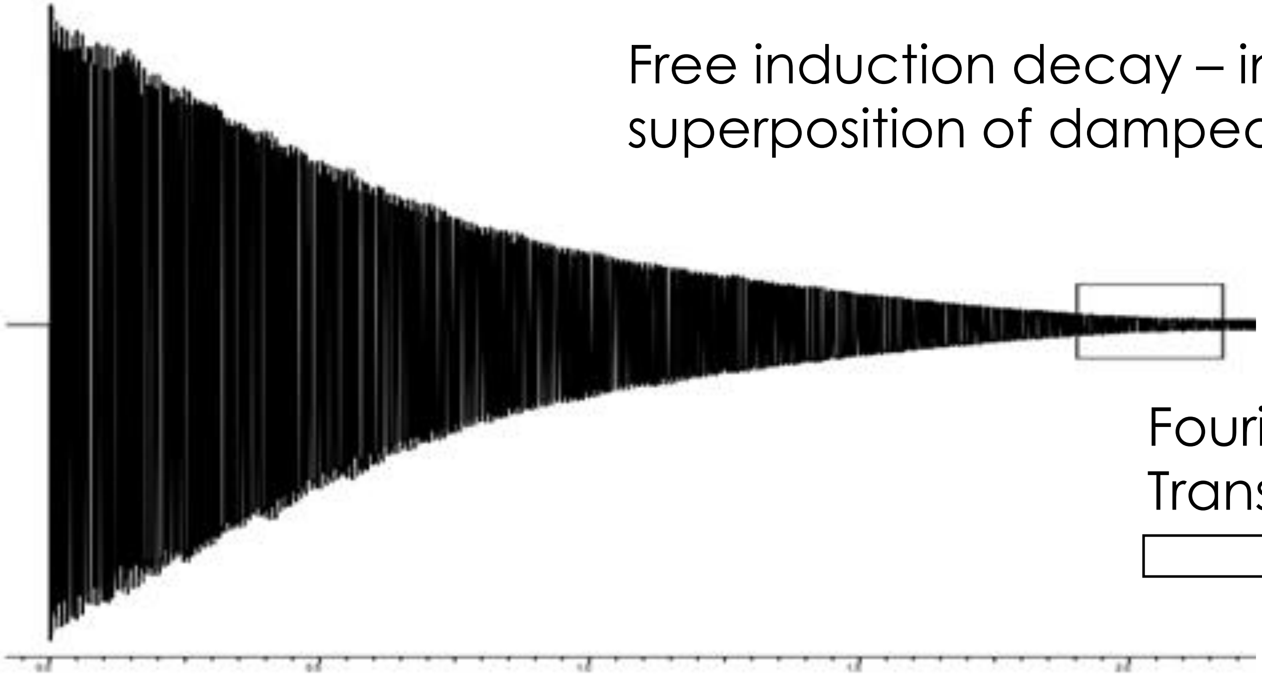
According to the uncertainty principle, a radio frequency field is generated over a wide range:
$\nu_0 \pm 1/\tau$

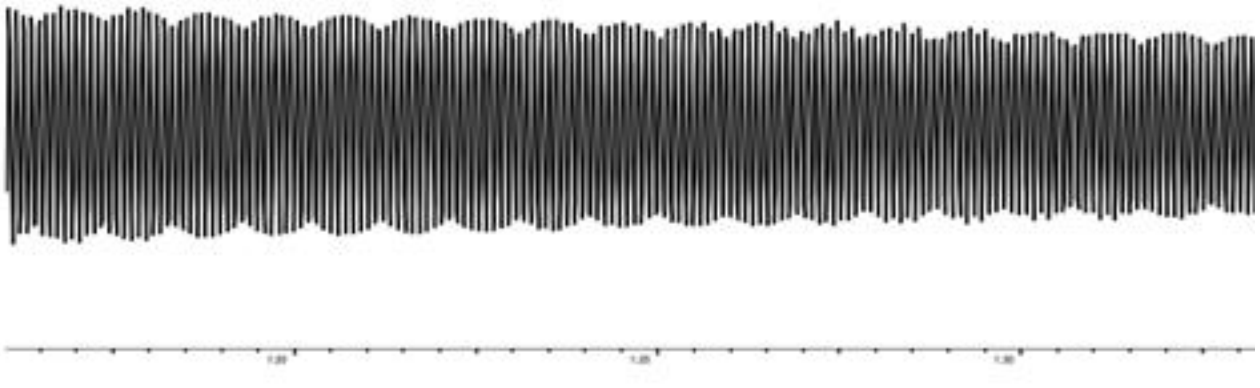


This work is funded by Russian Science Foundation (grant №23-23-00343).

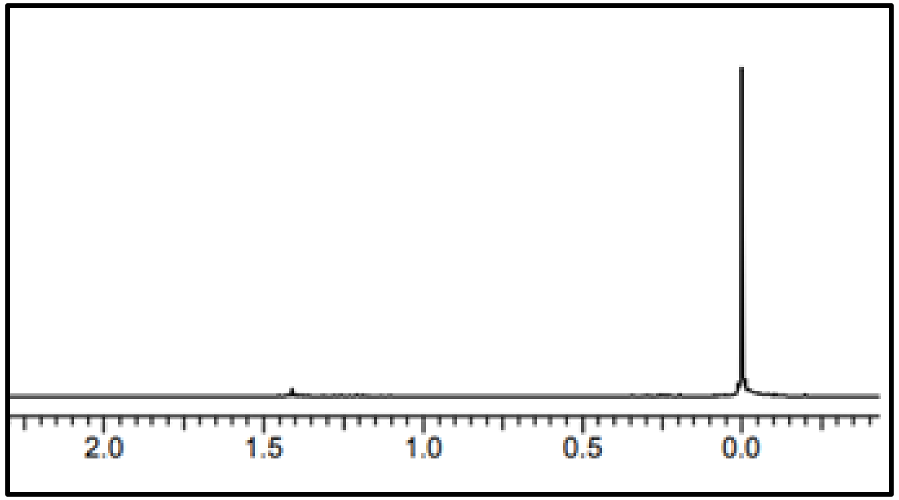
Pulse or Fourier-Transform NMR (FT-NMR)

Free induction decay – interferogram – superposition of damped harmonic oscillations





Fourier Transform



NMR spectrum

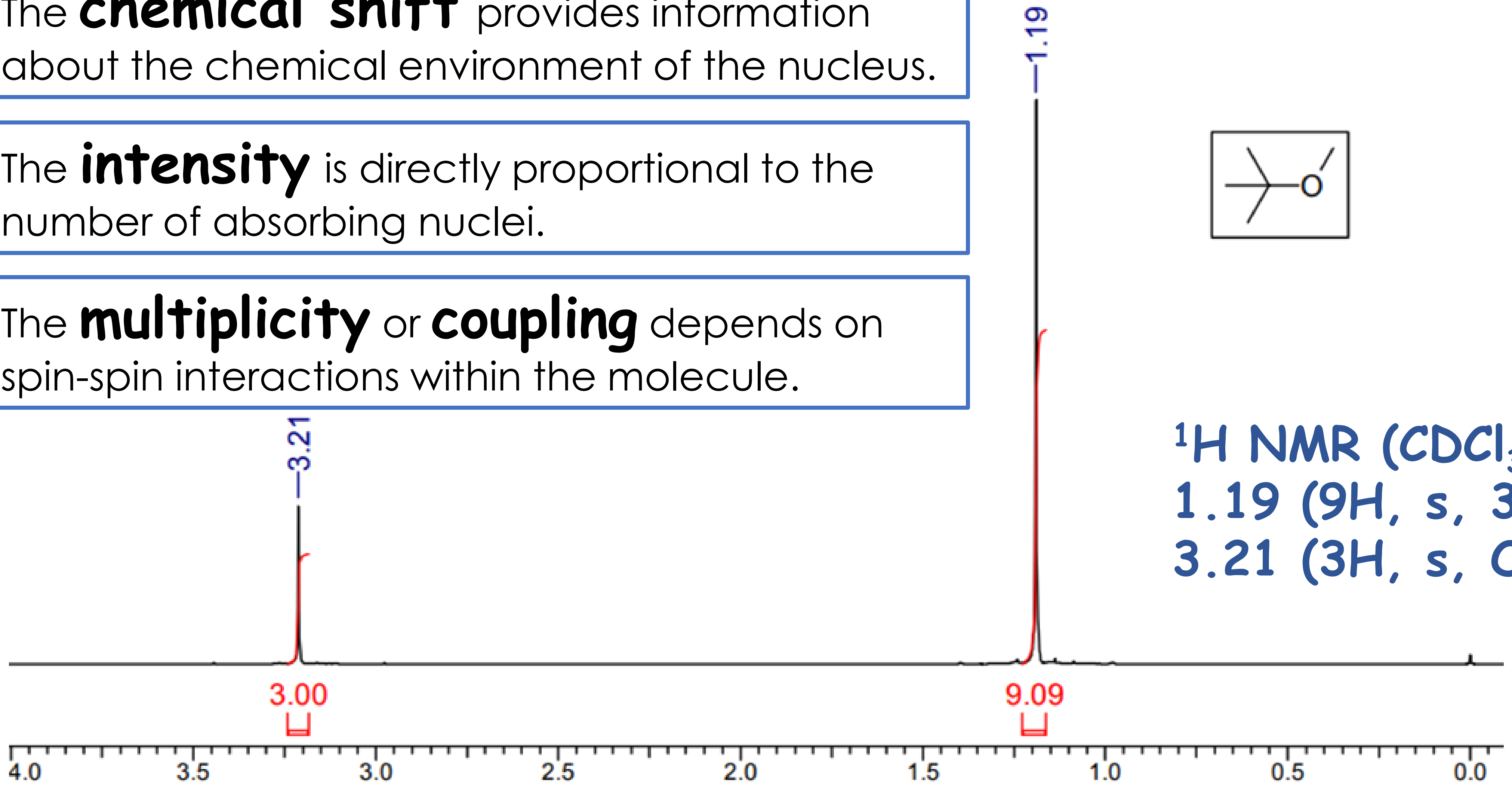
This work is funded by Russian Science Foundation (grant №23-23-00343).

Spectrum parameters of NMR

The **chemical shift** provides information about the chemical environment of the nucleus.

The **intensity** is directly proportional to the number of absorbing nuclei.

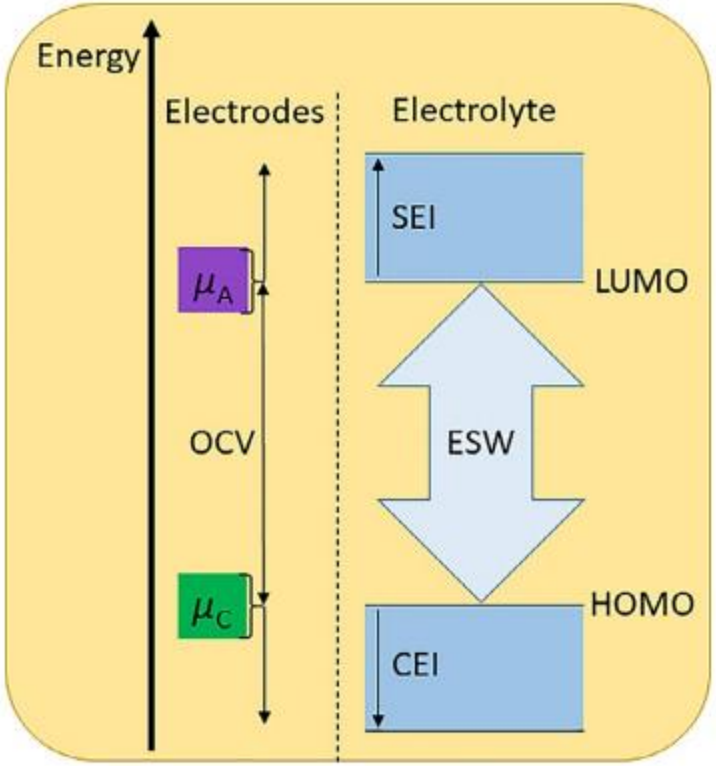
The **multiplicity** or **coupling** depends on spin-spin interactions within the molecule.



^{1}H NMR ($CDCl_3$) δ :
1.19 (9H, s, 3CH_3),
3.21 (3H, s, O-CH_3)

This work is funded by Russian Science Foundation (grant №23-23-00343).

Conventional organic electrolytes



Formulation:

- Lithium salt
- Organic solvent
- Additives

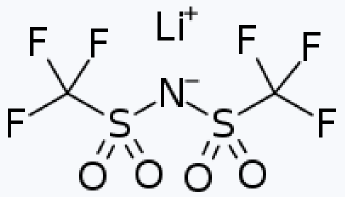
Advantages:

✓ High ionic conductivity
✓ …
✓ …

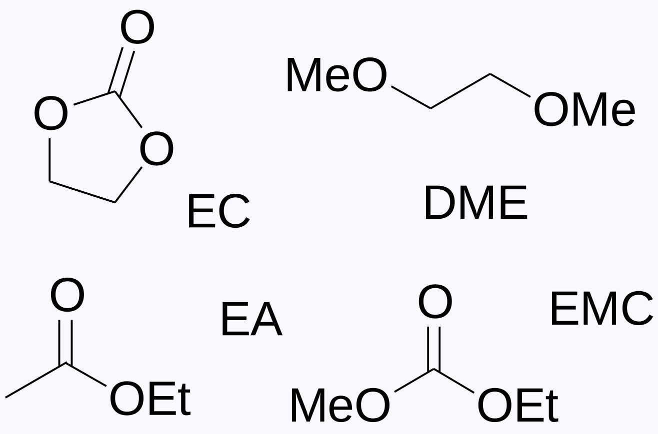
Salts

$LiPF_6$

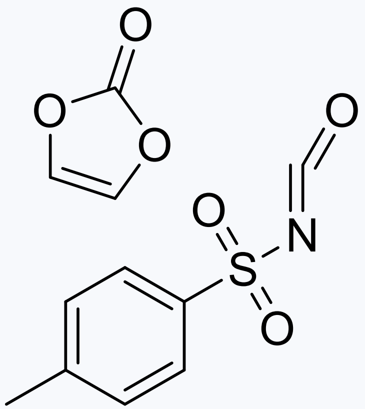
$LiBF_4$



Solvents



Additives



This work is funded by Russian Science Foundation (grant №23-23-00343).

Nuclei that can be studied by NMR

Spin quantum number = ½

Natural abundance ~100%

^{1}H, ^{19}F, ^{31}P

Spin quantum number = ½

Natural abundance <<100%

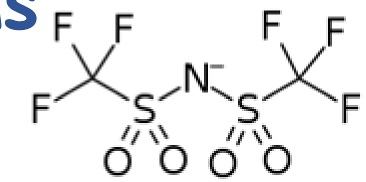
^{13}C

Spin quantum number > ½

^{7}Li (3/2), ^{23}Na (3/2)

Counterions

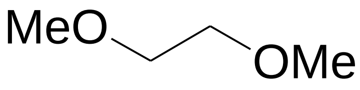
PF_6^-, BF_4^-,



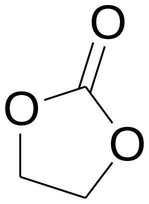
Ions

Li^+, Na^+

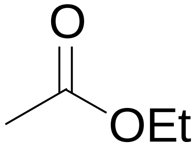
Solvents



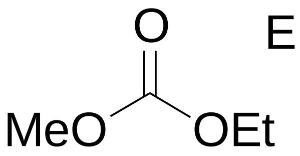
DME



EC



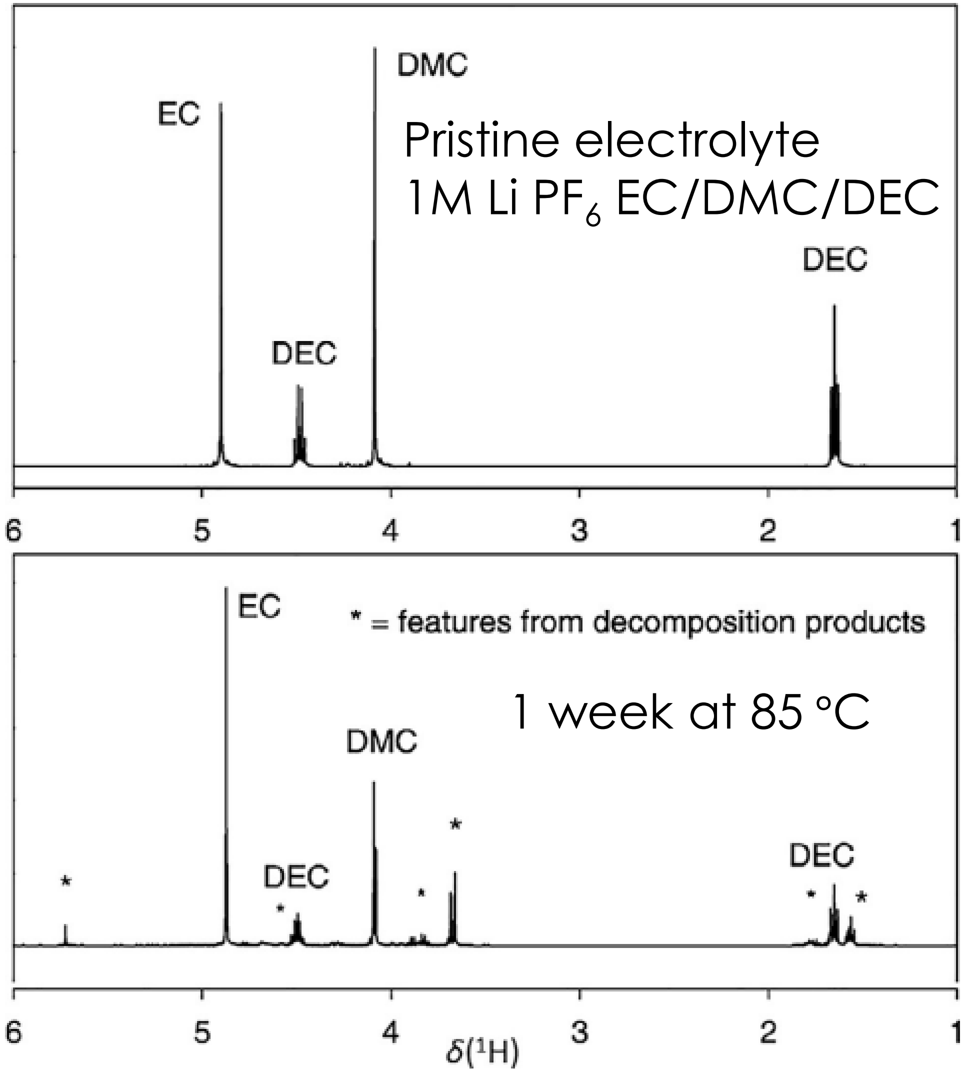
EA

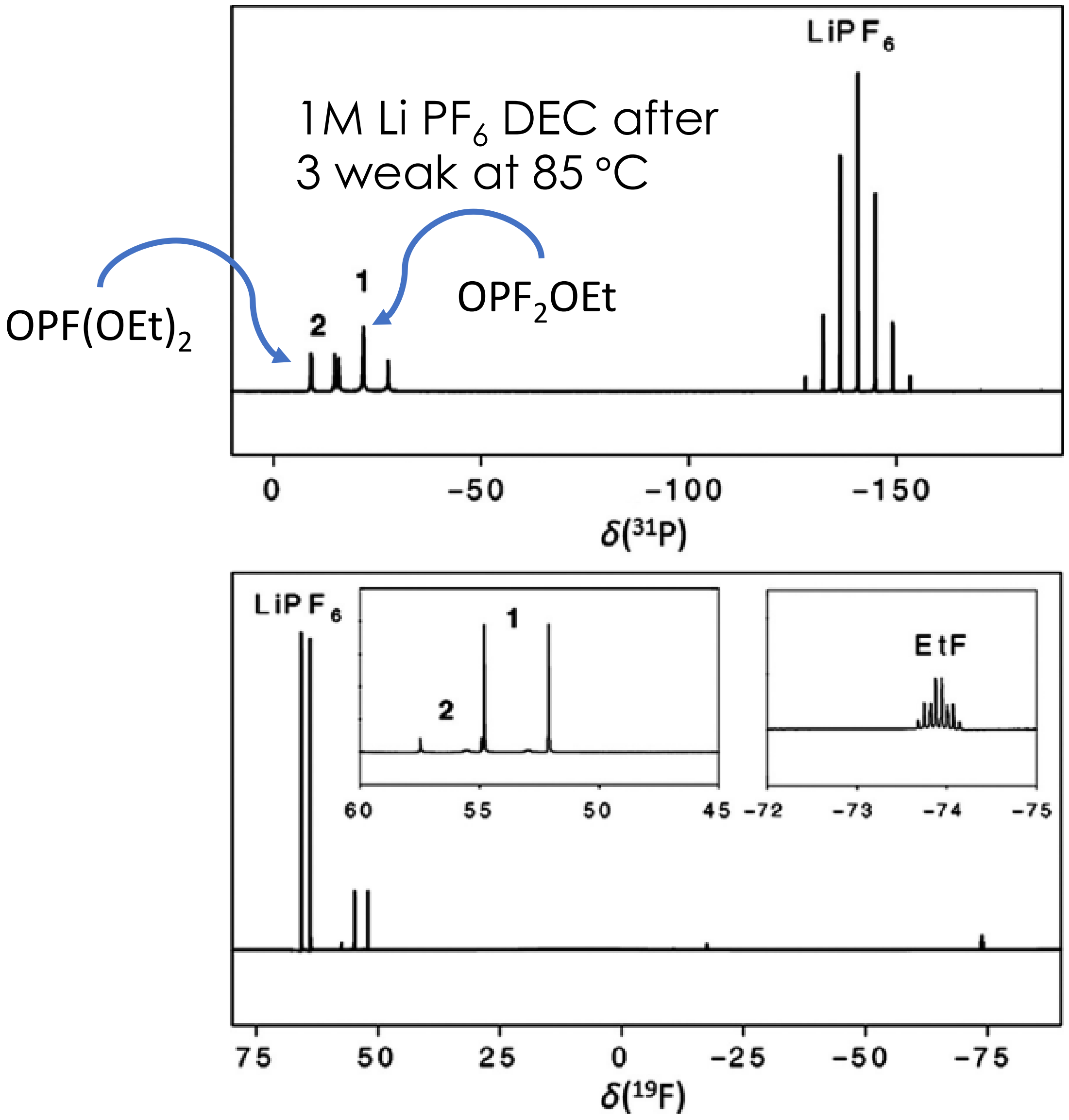


EMC

This work is funded by Russian Science Foundation (grant №23-23-00343).

Thermal stability of electrolytes

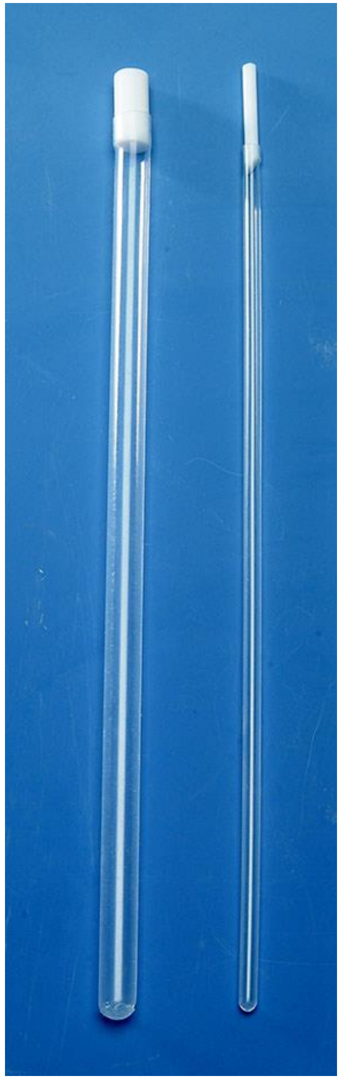




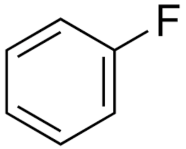
This work is funded by Russian Science Foundation (grant №23-23-00343).

Quantification of electrolyte degradation

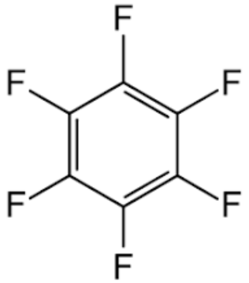
Polytetrafluoroethylene (PTFE) NMR tube

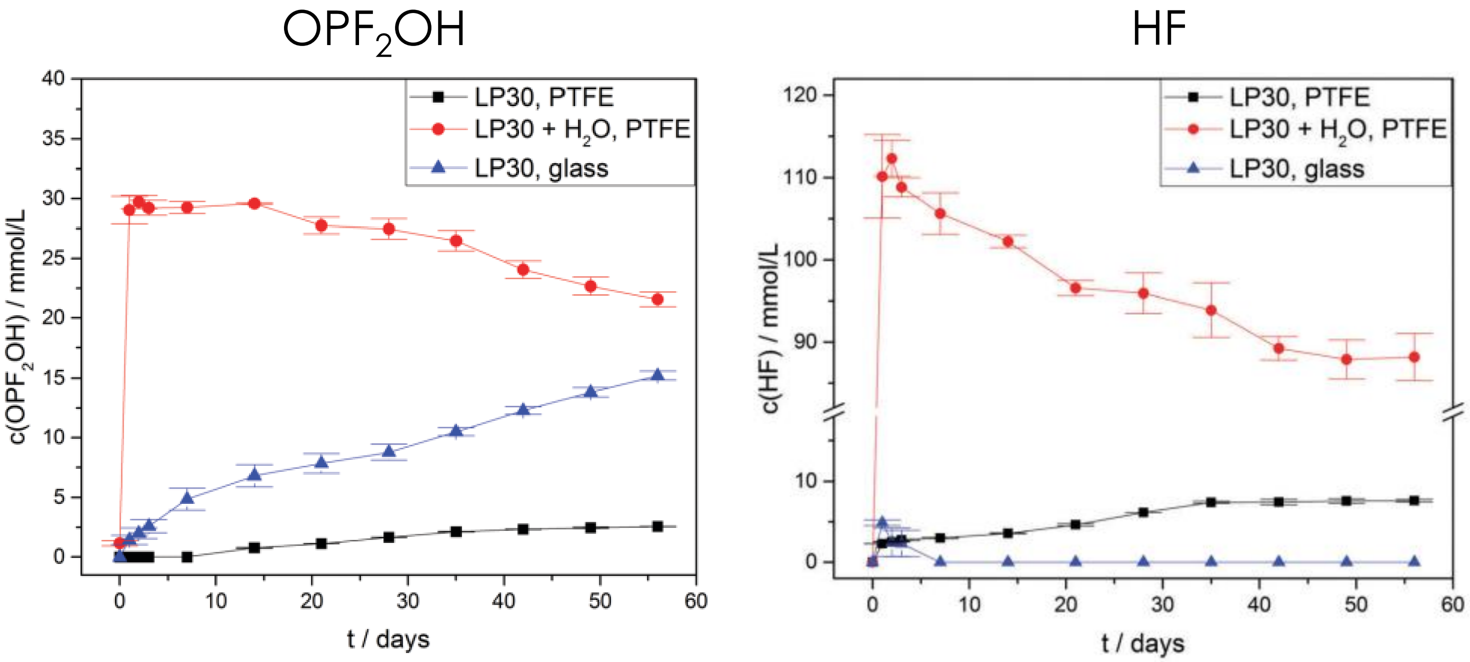


Internal standards



CF_3Cl



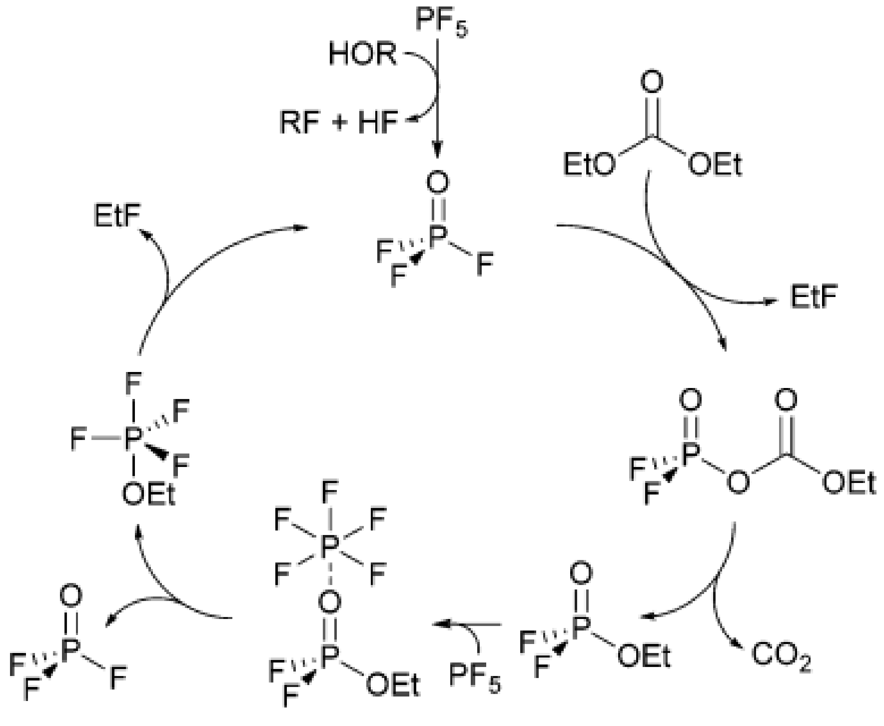


LP30 – 1M $LiPF_6$ in EC/DMC – 1/1

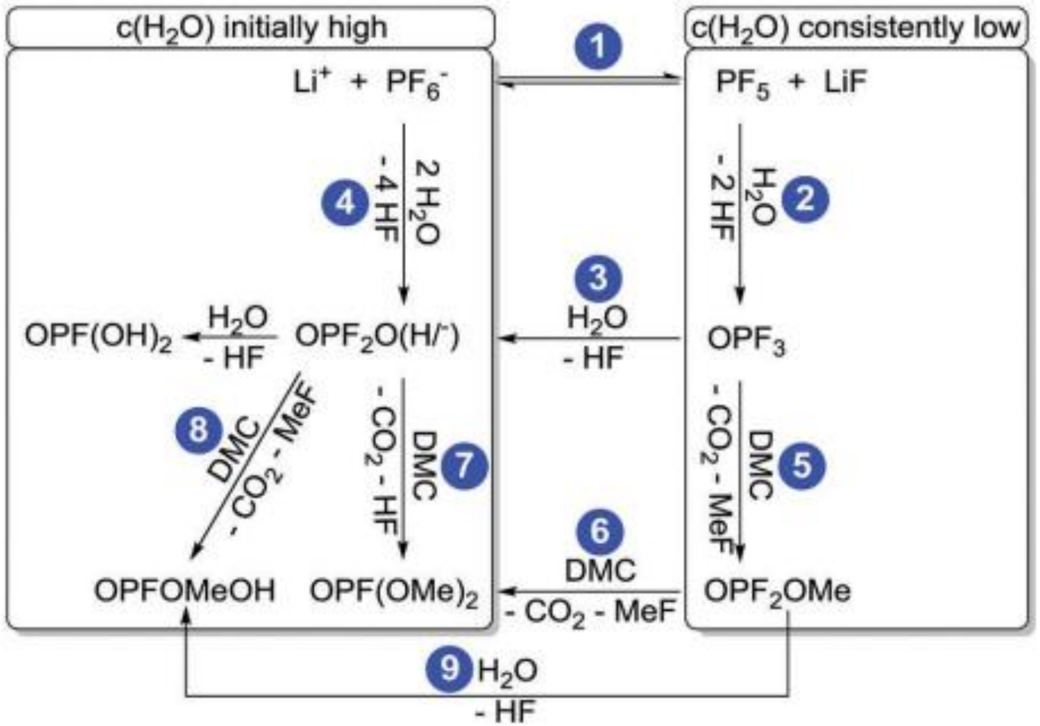
Samples were stored at 60°C

This work is funded by Russian Science Foundation (grant №23-23-00343).

Proposed reaction schemes for PF_6^- degradation



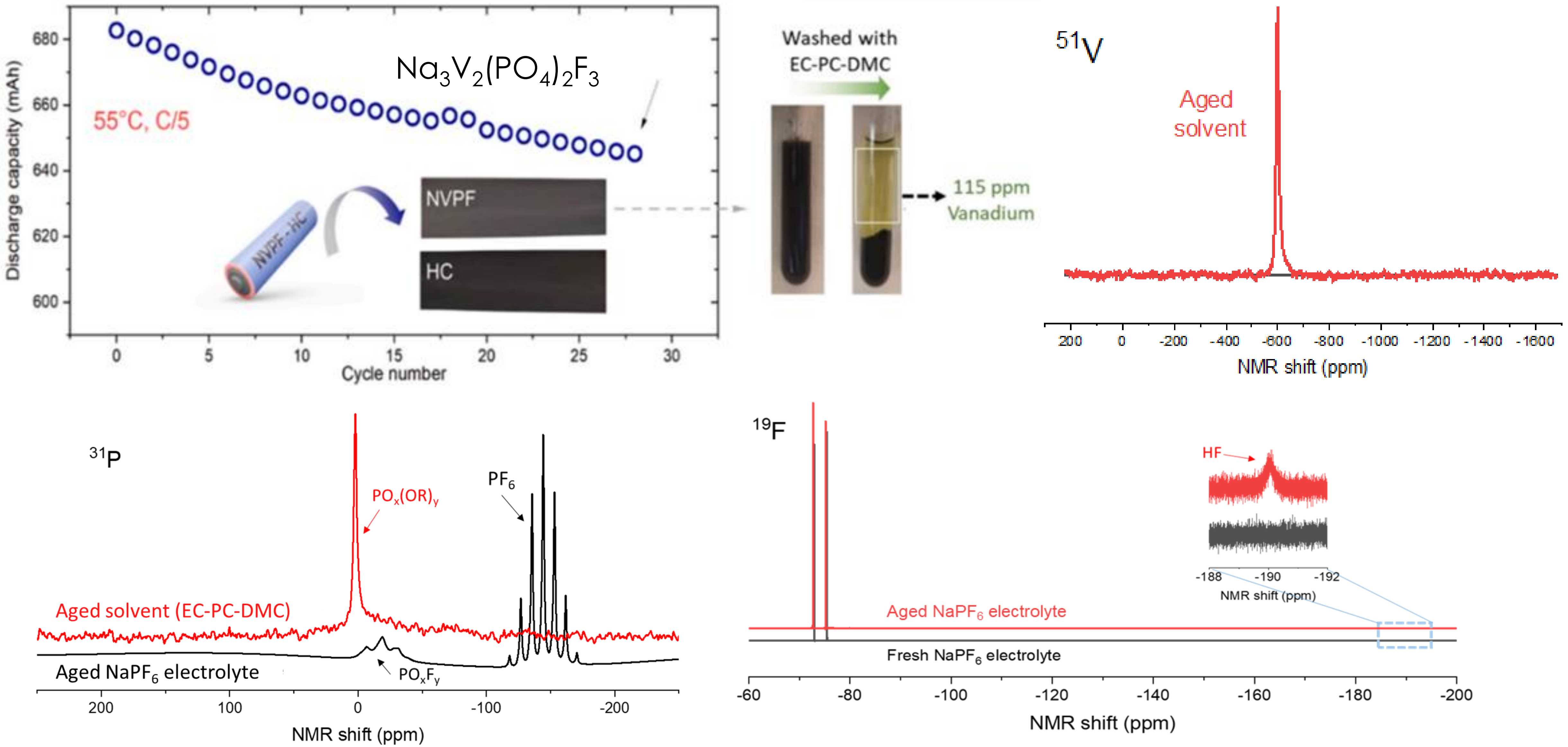
After studying in **glass** tubes



After studying in **polytetrafluoroethylene** tubes

This work is funded by Russian Science Foundation (grant №23-23-00343).

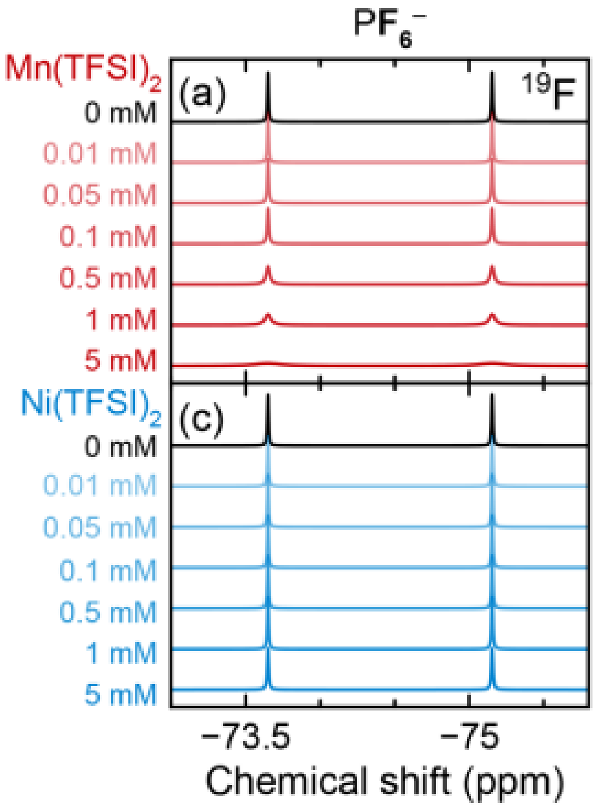
Cathode stability



This work is funded by Russian Science Foundation (grant №23-23-00343).

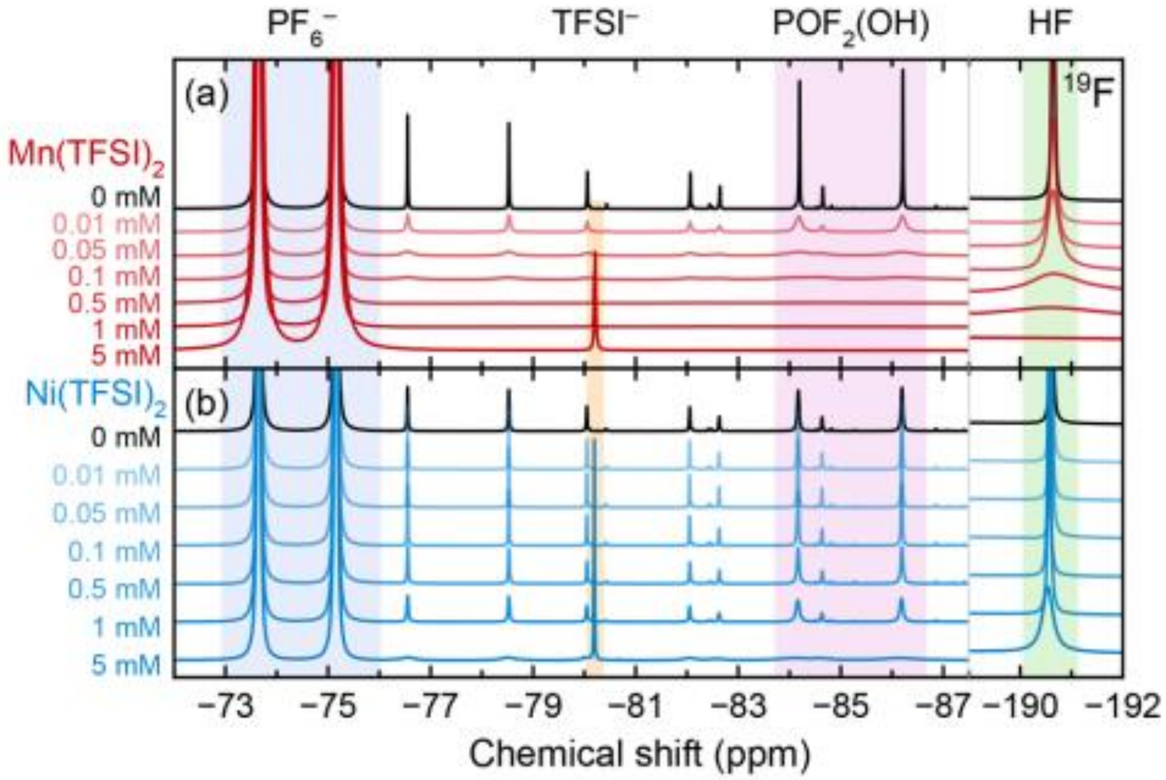
Spectral broadening caused by TM dissolution

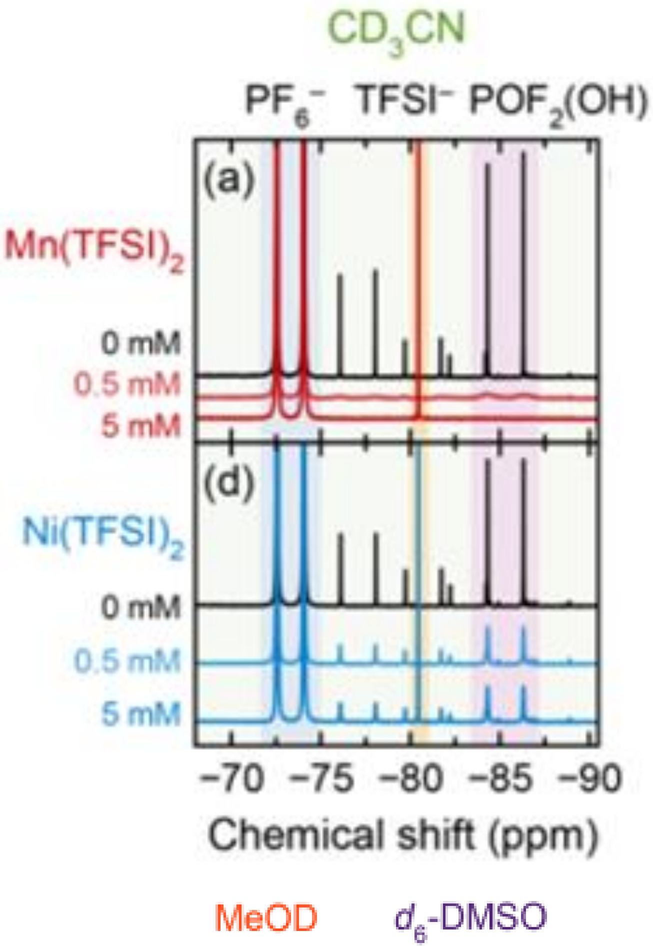
Pristine electrolyte



1M $LiPF_6$ in 3:7 EC/EMC

Degraded electrolytes

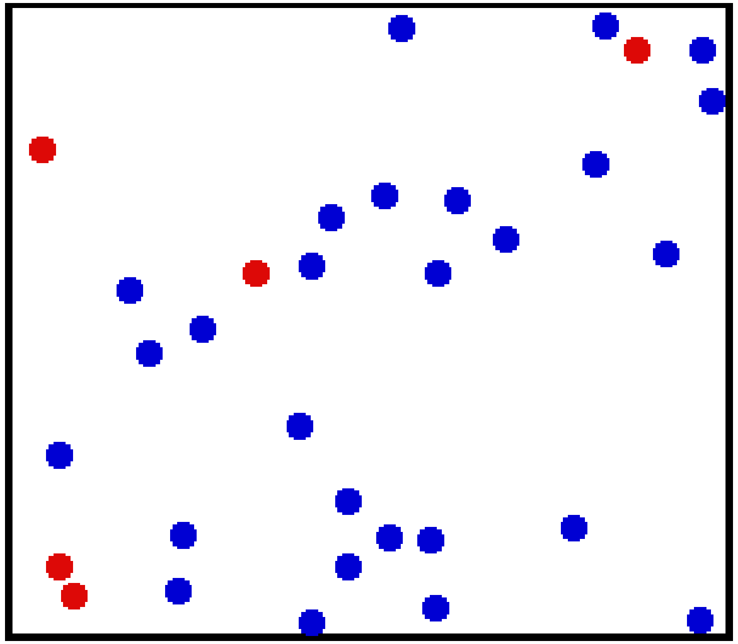




Li_3PO_4

This work is funded by Russian Science Foundation (grant №23-23-00343).

DOSY Diffusion-Ordered Spectroscopy



Stoke-Einstein Equation

$$D = \frac{k_b T}{6\pi\eta r_h}$$

Unit = m^2/sec

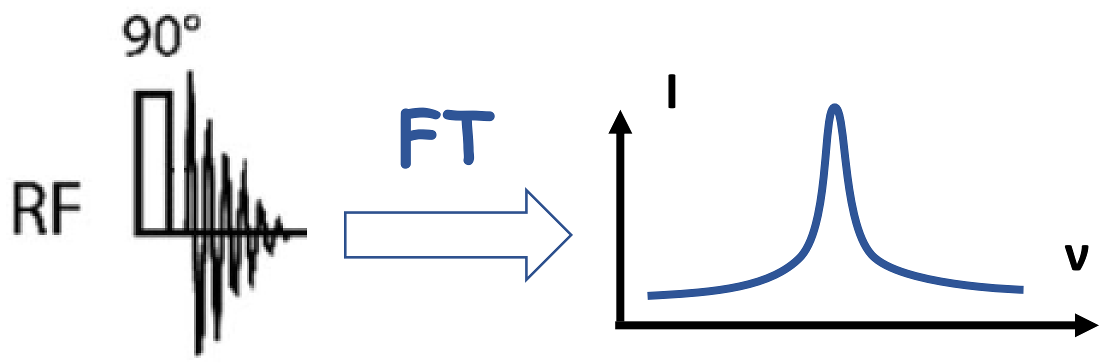
D – Diffusion coefficient
k_b – Boltzmann constant (1.380649×10^{-23} J·K^{-1})
T – Temperature
η – Viscosity
r_h – Hydrodynamic radius

Root mean square displacement

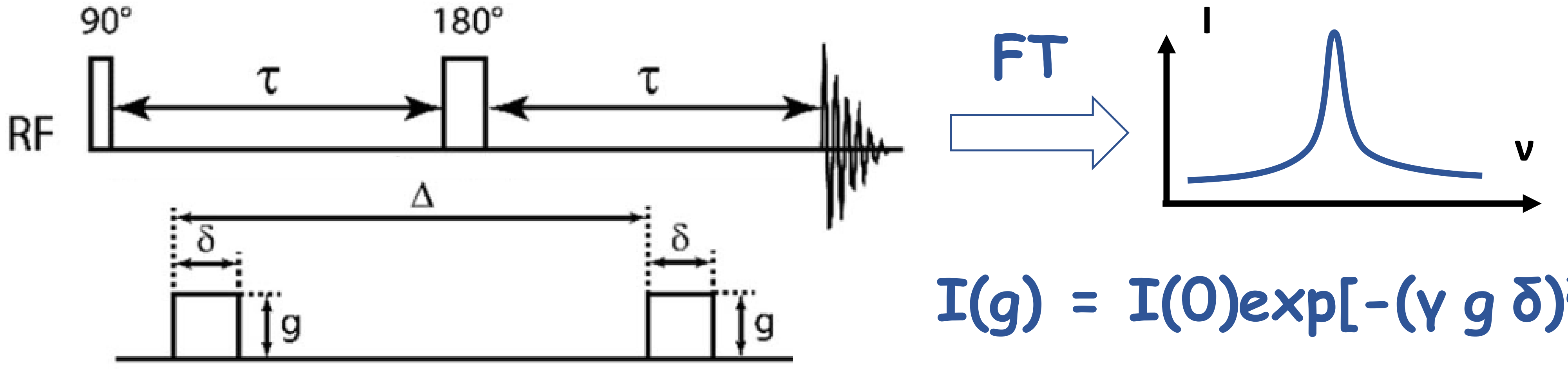
$$\overline{S} = \sqrt{6DT}$$

This work is funded by Russian Science Foundation (grant №23-23-00343).

DOSY Diffusion-Ordered Spectroscopy



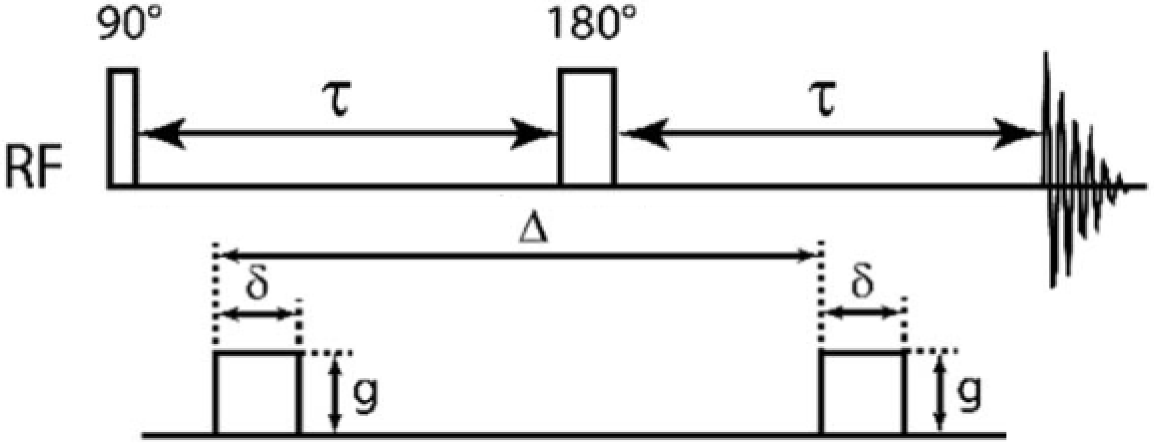
Spin echo + pulsed fiends gradient



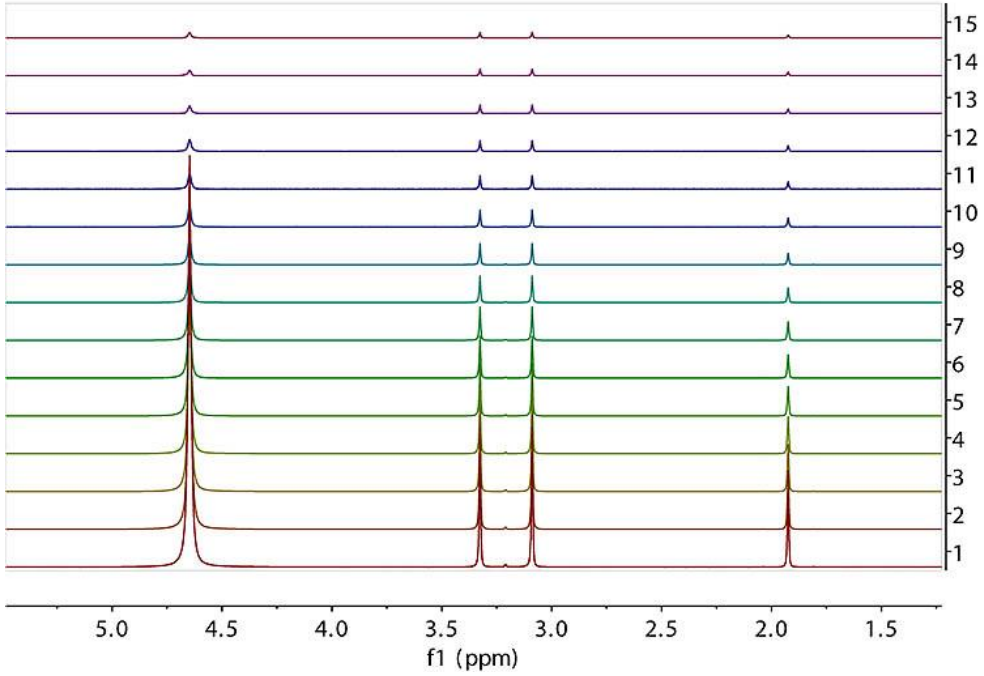
$$I(g) = I(0)\exp[-(\gamma\, g\, \delta)^2 D(\Delta - \frac{\delta}{3})]$$

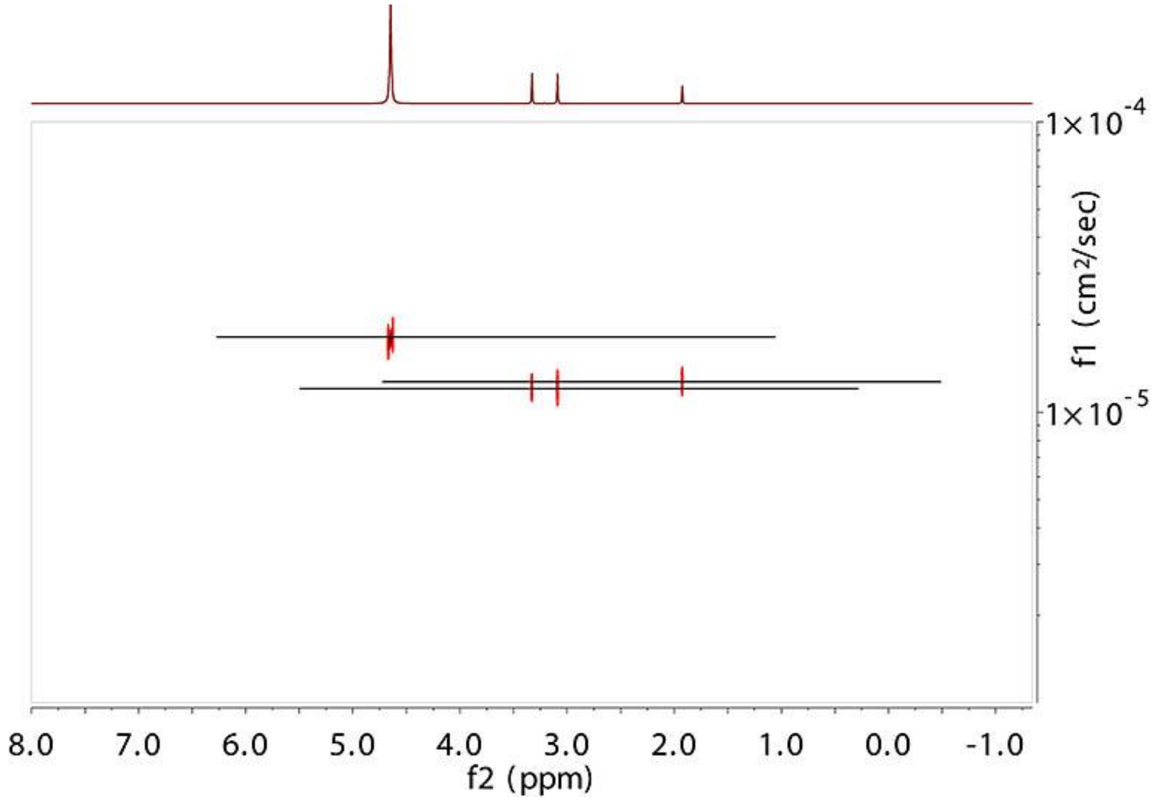
This work is funded by Russian Science Foundation (grant №23-23-00343).

Schematic principle of DOSY NMR



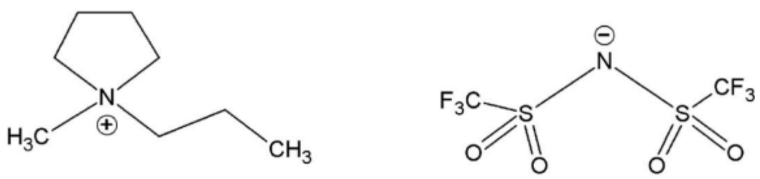
$$I(g) = I(0)\exp[-(\gamma\, g\, \delta)^2 D(\Delta - \frac{\delta}{3})]$$



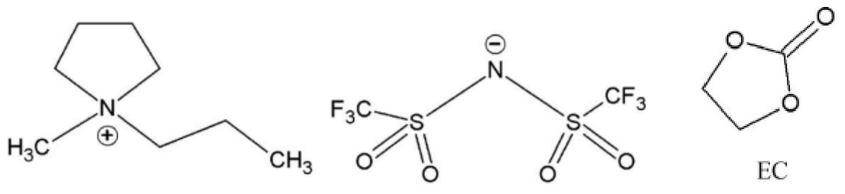


This work is funded by Russian Science Foundation (grant №23-23-00343).

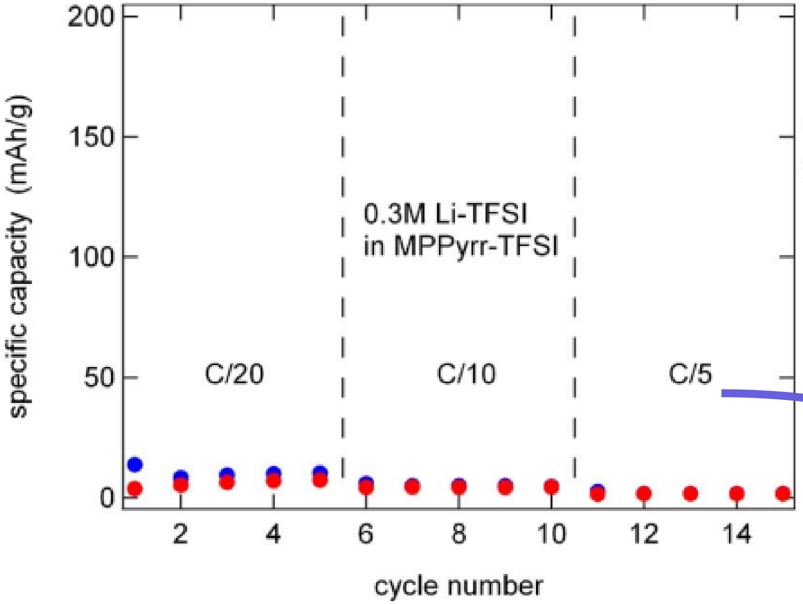
Ion mobility and battery performance

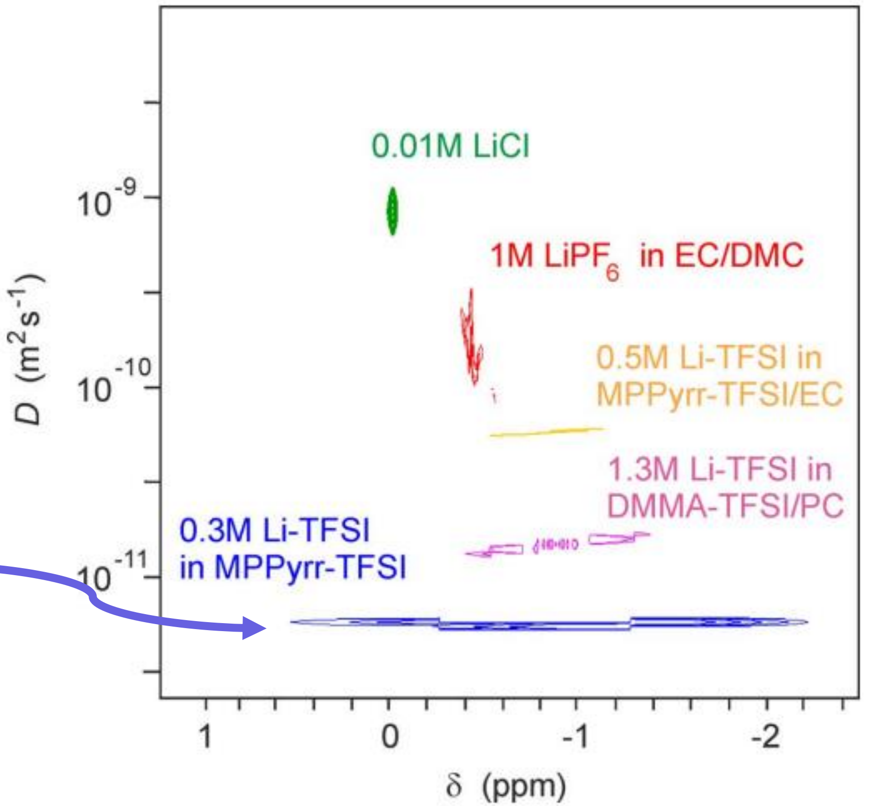


^{7}Li DOSY NMR spectra of different electrolytes

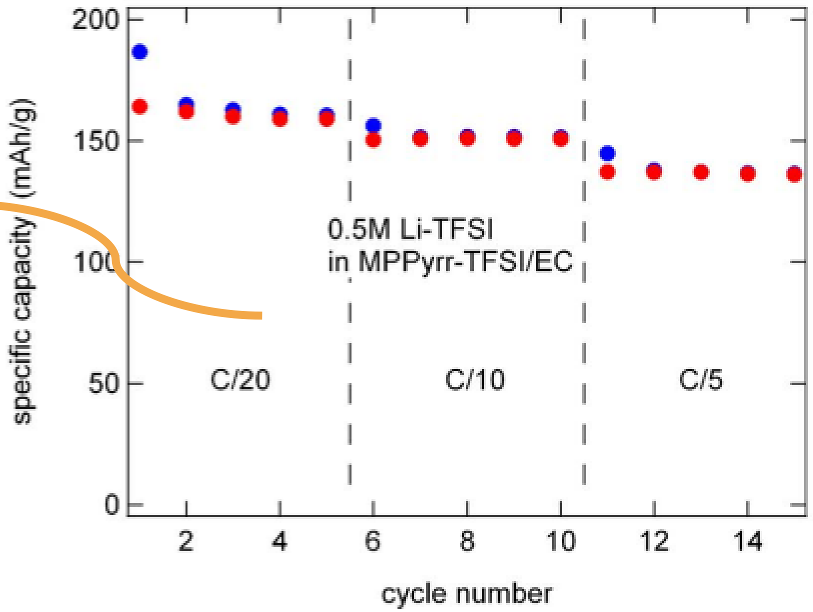


MPPyrr-TFSI





MPPyrr-TFSI/EC

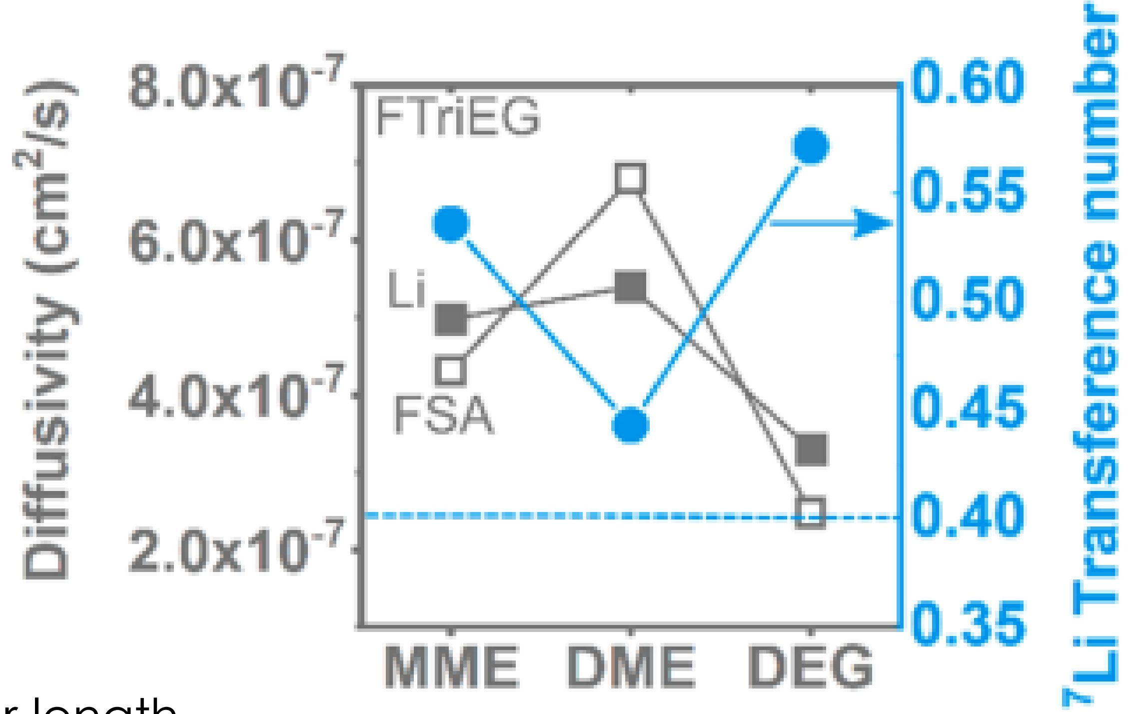


This work is funded by Russian Science Foundation (grant №23-23-00343).

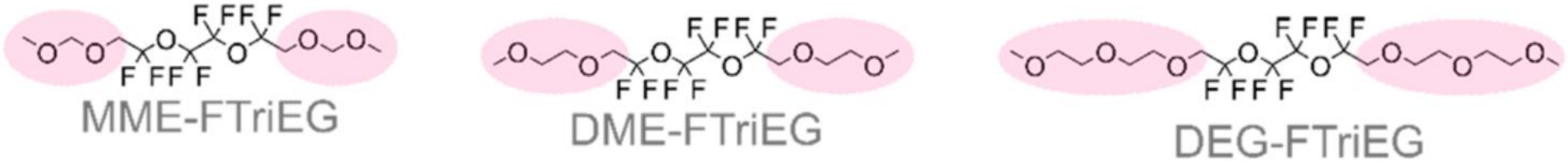
Ion transport number

$$t_{Li^+} \approx \frac{D_{Li^+}}{D_{Li^+} + D_{FSI^-}}$$

0.1M LiFSI

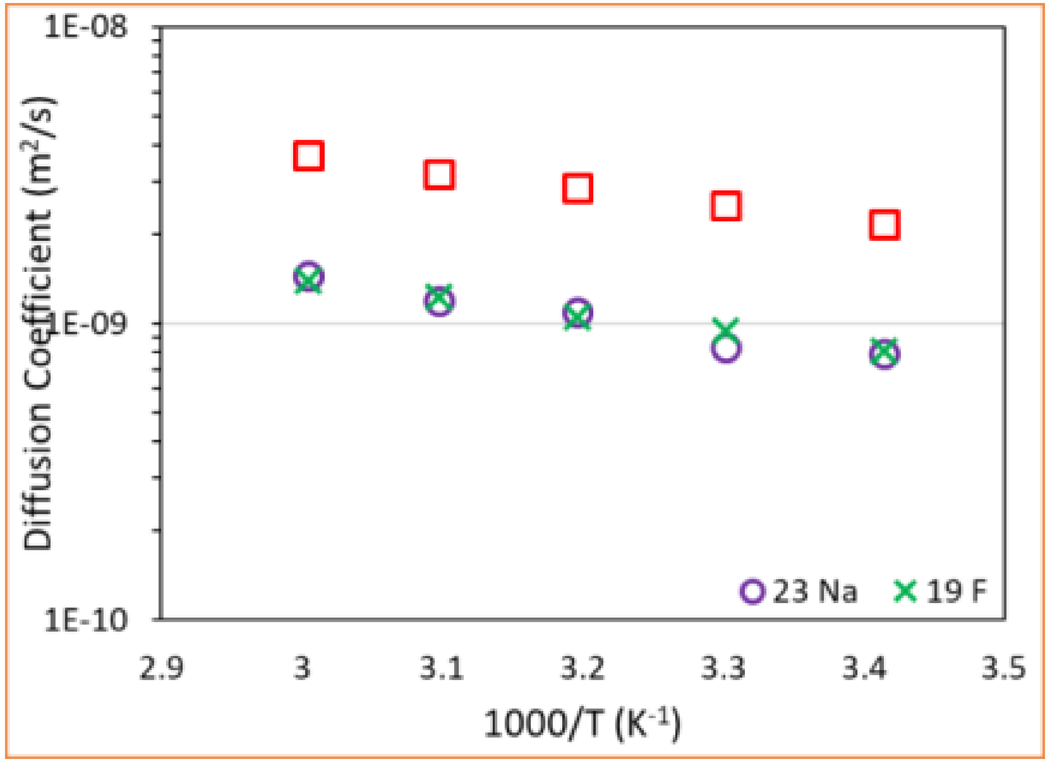


Increasing ether length

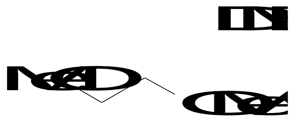


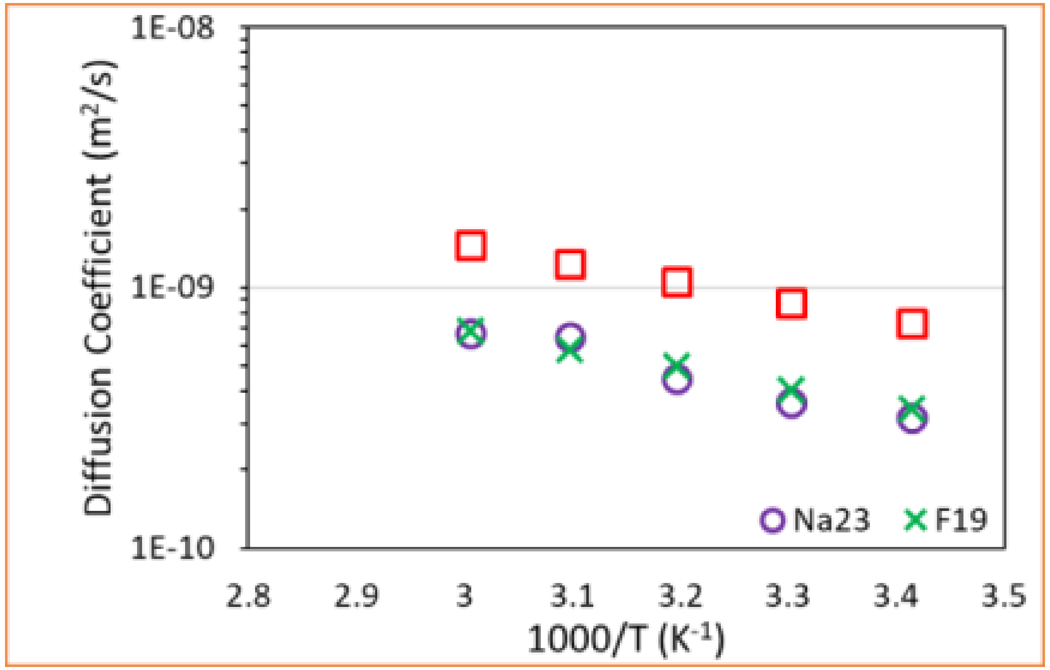
This work is funded by Russian Science Foundation (grant №23-23-00343).

Ion mobility and battery performance

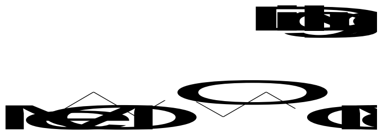


1M NaTFSI



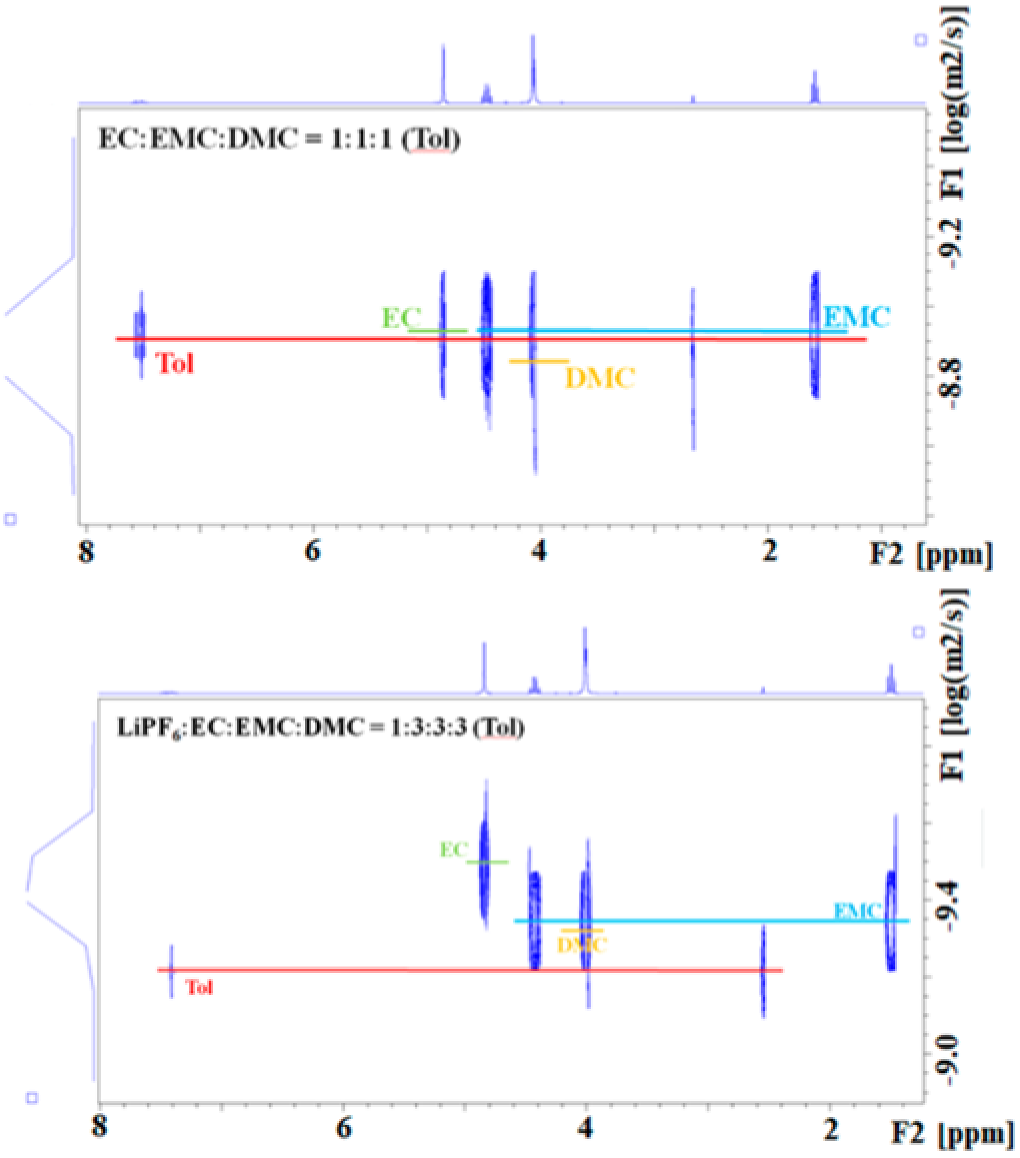


1M NaTFSI



This work is funded by Russian Science Foundation (grant №23-23-00343).

Internally referenced DOSY-NMR



2 DOSY experiments with toluene as an **internal** reference
1) Solvents without $LiPF_6$
2) Solvents + $LiPF_6$

D_{1tol}, D_{2tol}, D_{Li}, D_{1EMC}, D_{2EMC}

Stoke-Einstein equation

$$D = \frac{k_b T}{6\pi\eta r_h}$$

This work is funded by Russian Science Foundation (grant №23-23-00343).

Internally referenced DOSY-NMR

Divulging the solution structure of lithium-ion battery electrolytes

Stoke-Einstein equation

$$D = \frac{k_b T}{6\pi\eta r_h}$$

$D_{\text{Observed EMC}} = a^*D_{\text{Coordinated-EMC}} + (1 - a)D_{\text{free-EMC}}$

$D_{\text{Coordinated EMC}} = D_{Li^+}$

a – the ratio of coordinated EMC

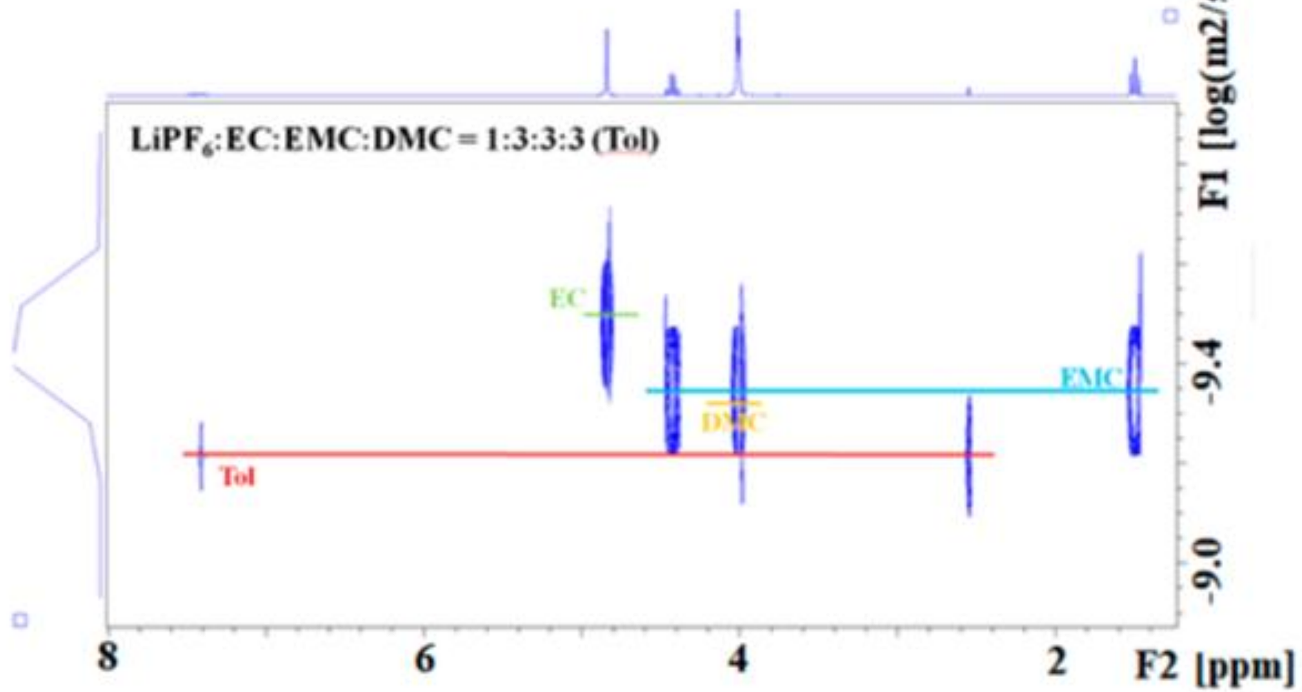
$$\frac{D_{1T}}{D_{2T}} = \frac{\dfrac{kT_1}{6\pi\eta_1 r}}{\dfrac{kT_2}{6\pi\eta_2 r}} = \boxed{\frac{T_1\eta_2}{T_2\eta_1}}$$

$$D_{\text{Free-EMC}} = \frac{\dfrac{kT_1}{6\pi\eta_1 r_{1E}}}{\dfrac{kT_2}{6\pi\eta_2 r_{1E}}} D_{1EMC} = \boxed{\frac{T_1\eta_2}{T_2\eta_1}} D_{1EMC}$$

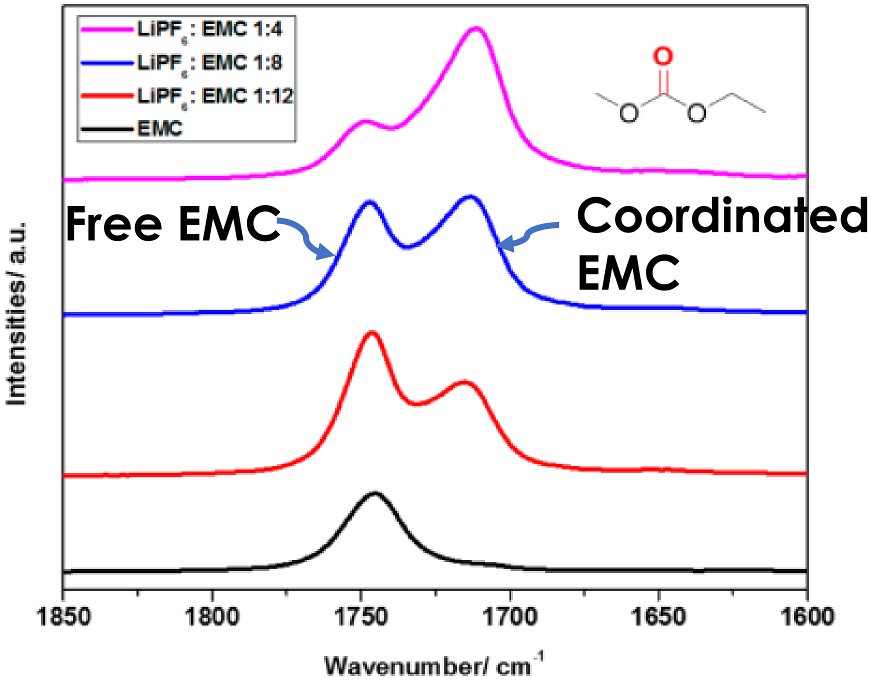
This work is funded by Russian Science Foundation (grant №23-23-00343).

The solution structure of electrolytes

New method



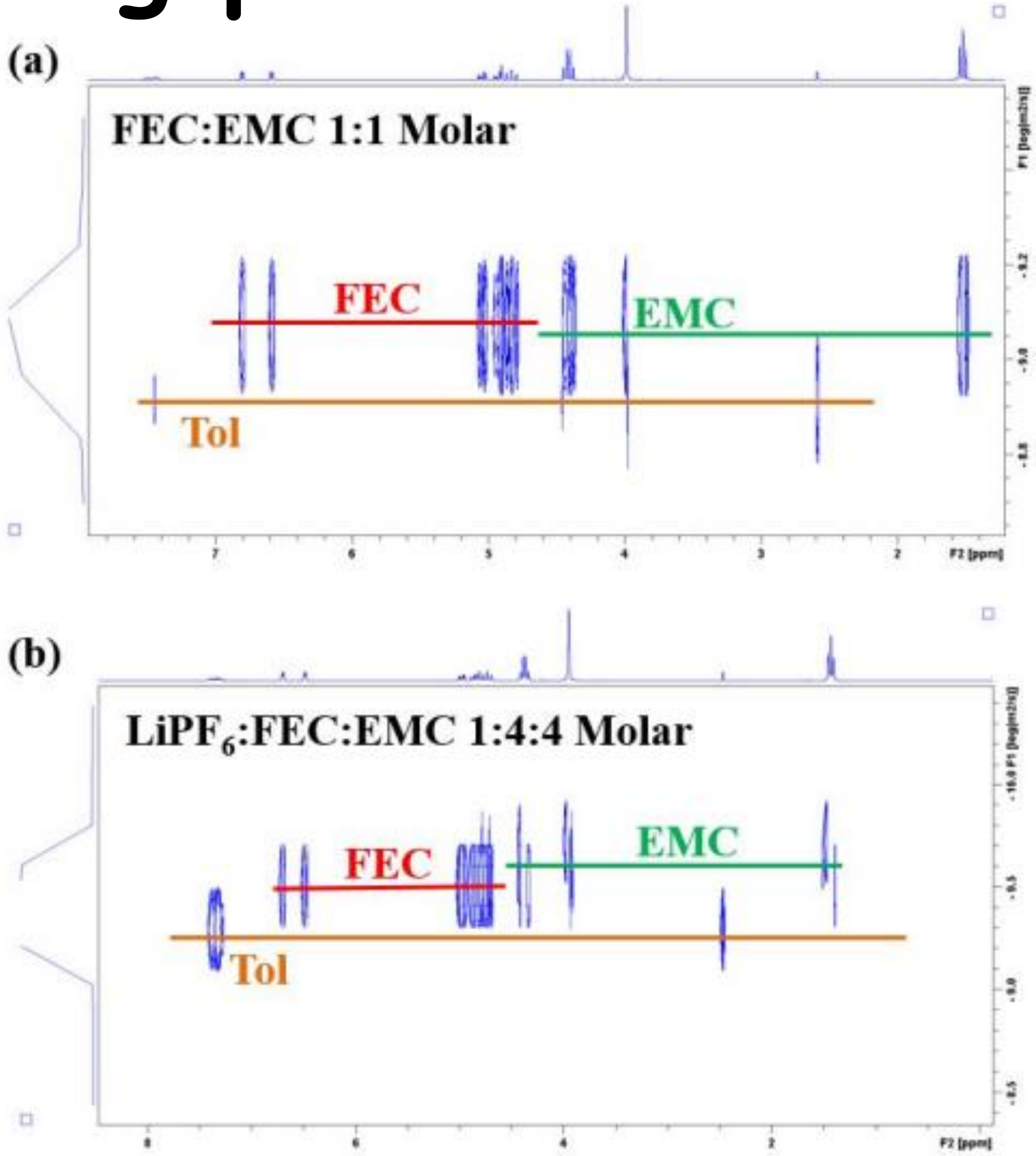
Old method



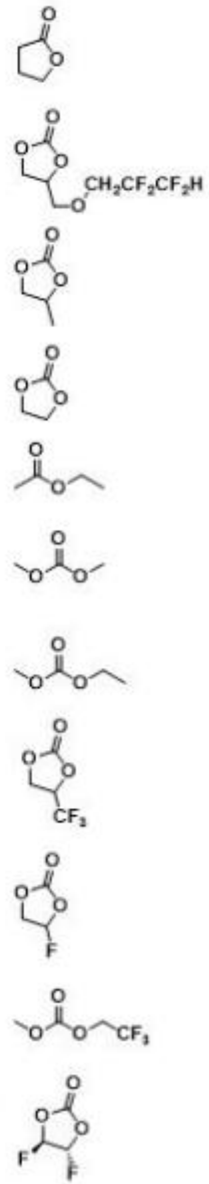
electrolyte	coordination ratio α^b	coordination number of Li[b,c]	coordination ratio α by FTIR
$LiPF_6$:EMC 1:12	0.45 ± 0.01	5.4 ± 0.1	0.46
$LiPF_6$:EMC 1:8	0.56 ± 0.01	4.5 ± 0.1	0.57
$LiPF_6$:EMC 1:4	0.74 ± 0.02	3.0 ± 0.1	0.72

This work is funded by Russian Science Foundation (grant №23-23-00343).

Solvating power of solvents



$$\chi = \frac{\alpha_{ES}}{\alpha_{EMC}}$$

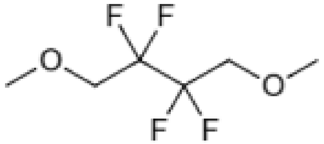


Solvent	χ
GBL	1.95
HFEEC	1.82
PC	1.46
EC	1.41
EA	1.17
DMC	1.02
EMC	1
TFPC	0.83
FEC	0.63
FEMC	0.44
DFEC	0.10

This work is funded by Russian Science Foundation (grant №23-23-00343).

Solvent characterization

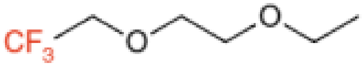
Coordinating solvent number (1.2M LiFSI)



1.77

2.20

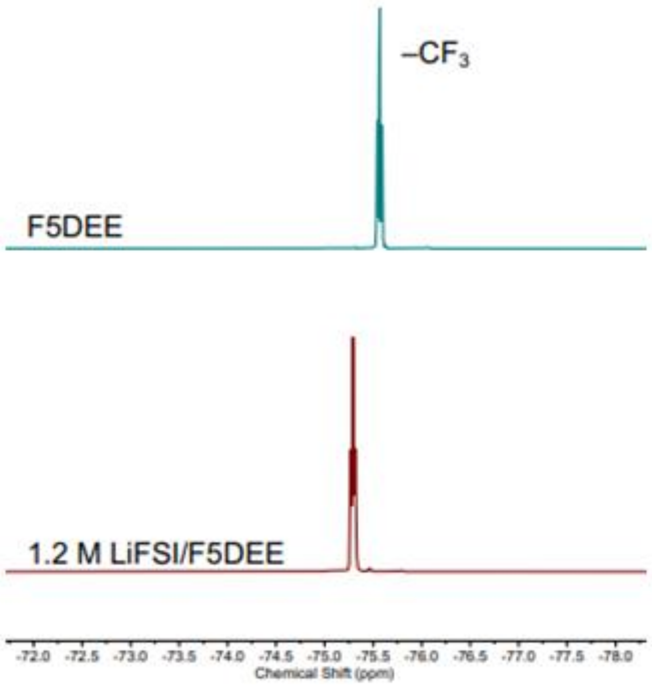
1.57

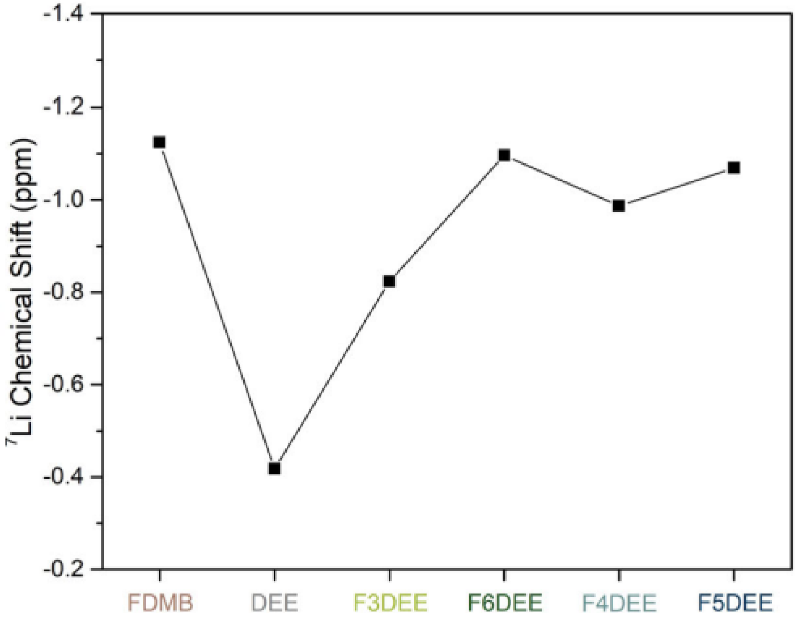


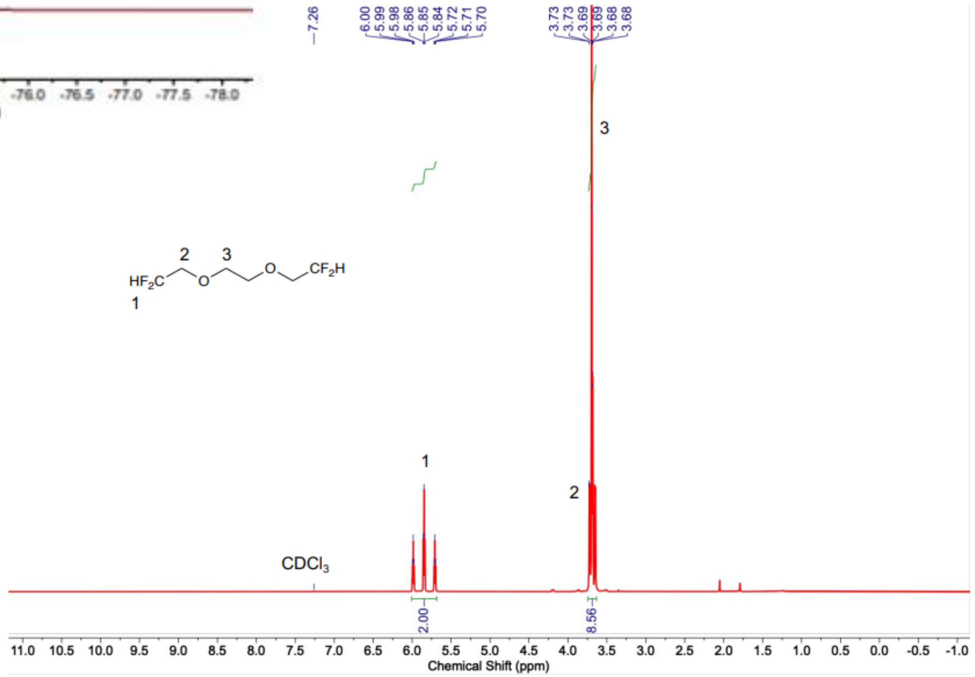
2.19

2.06

2.20

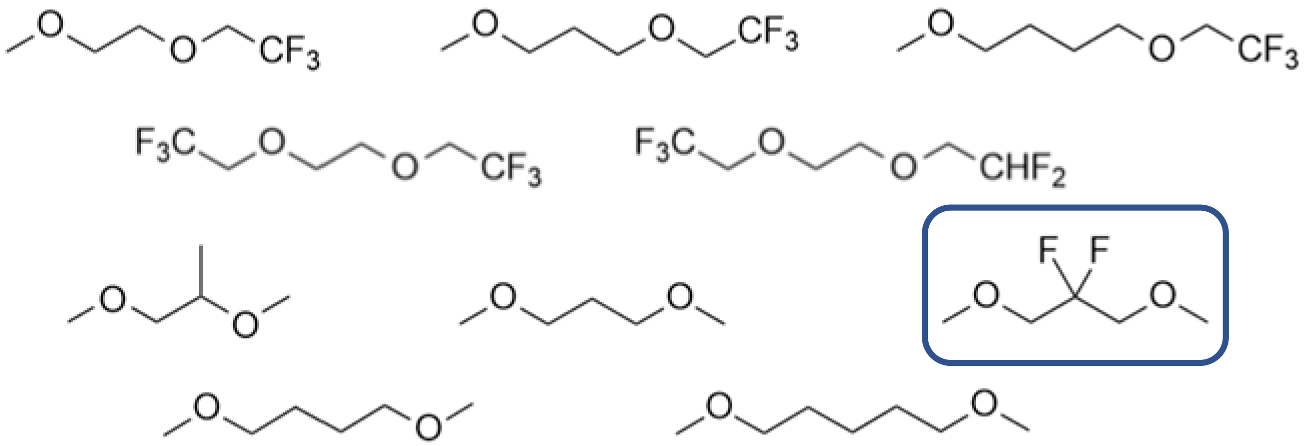


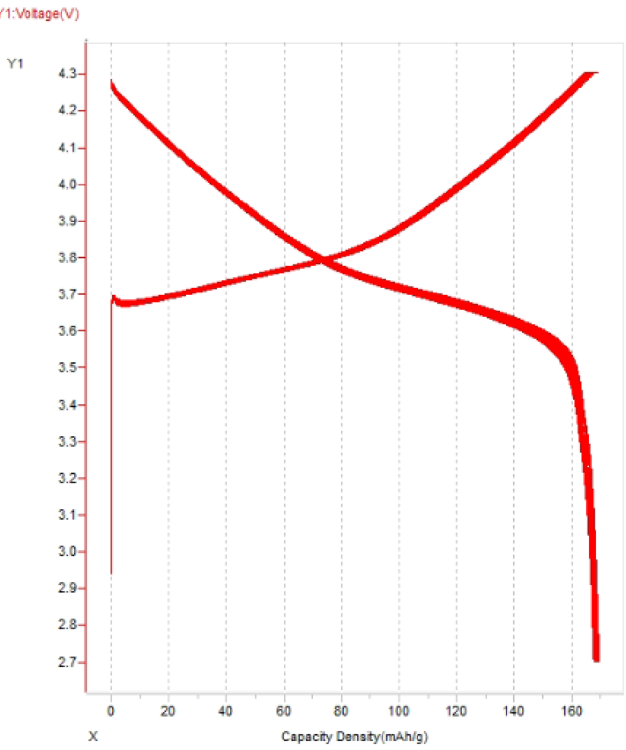


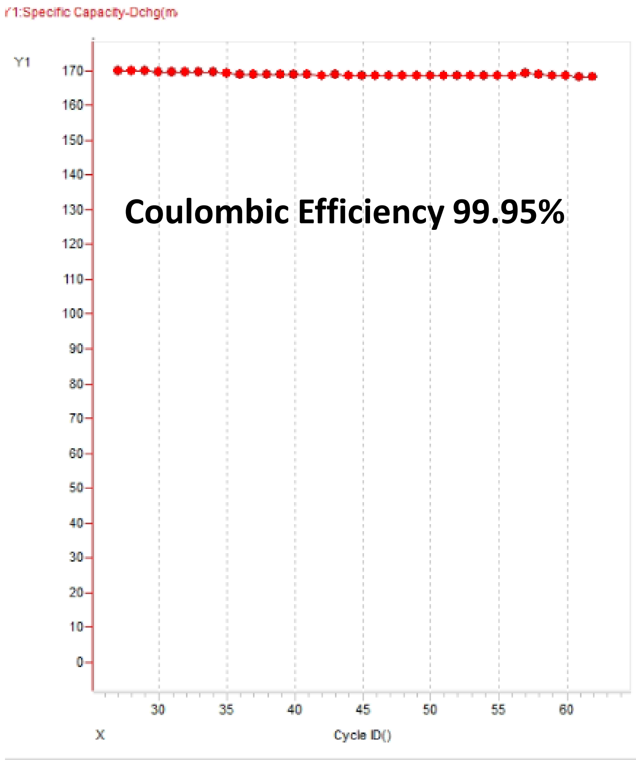


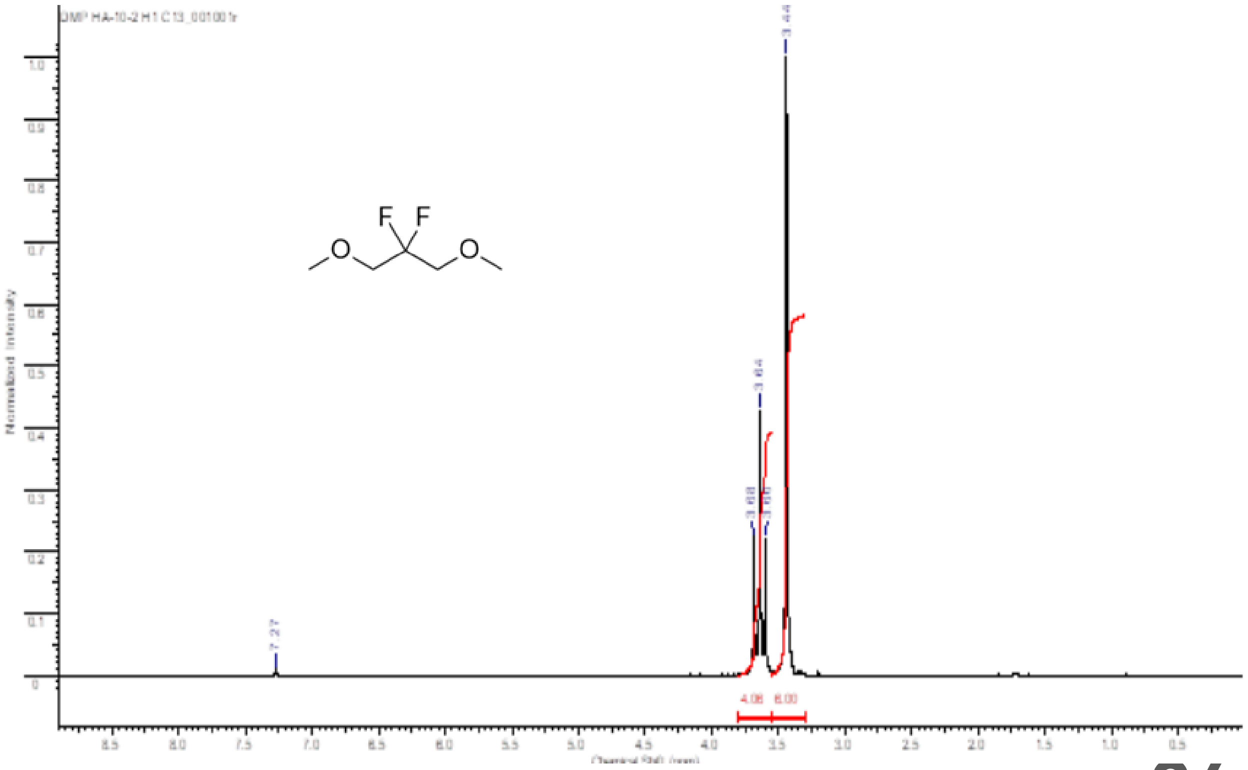
This work is funded by Russian Science Foundation (grant №23-23-00343).

Our advances in electrolyte design









This work is funded by Russian Science Foundation (grant №23-23-00343).

Thx!