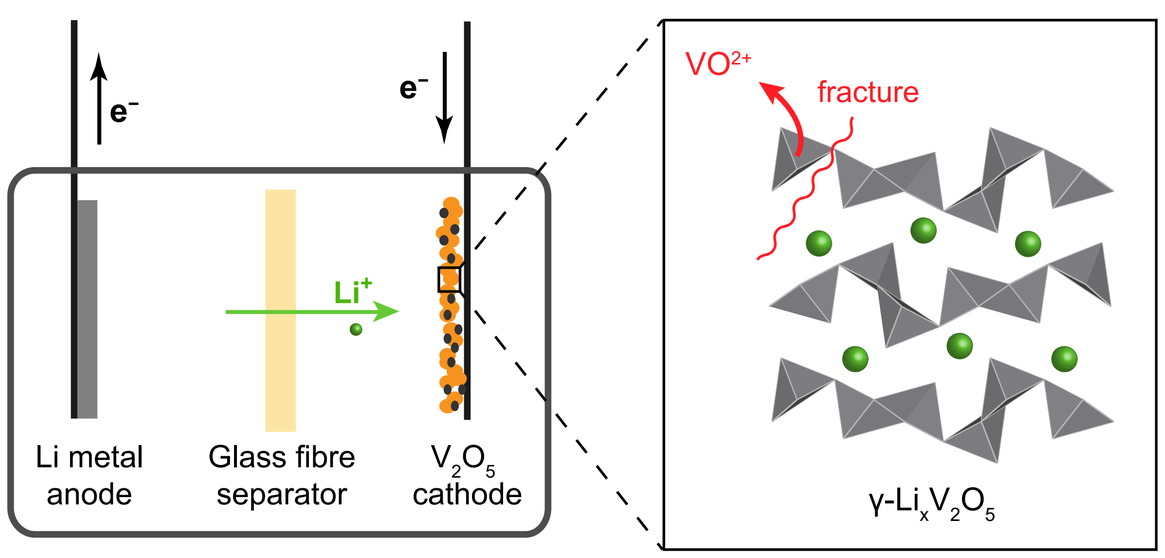
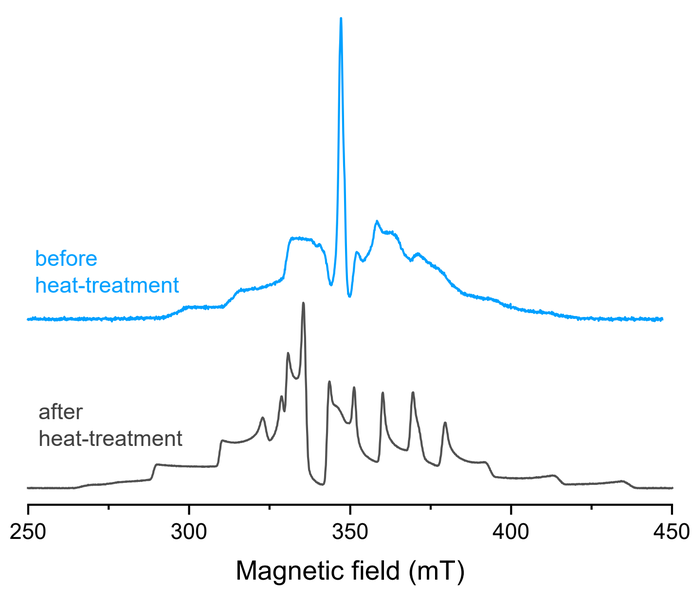
Using vanadyl sensors to investigate electrolyte degradation in Li-ion batteries

Conrad Szczuka[a,b], Peter Jakes[a], Rüdiger-A. Eichel[a,b] and Josef Granwehr[a,c]

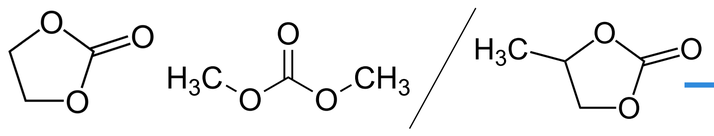
[a]*Institute of Energy and Climate Research (IEK-9), Forschungszentrum Jülich, Jülich, Germany*
[b]*Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany*
[c]*Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*



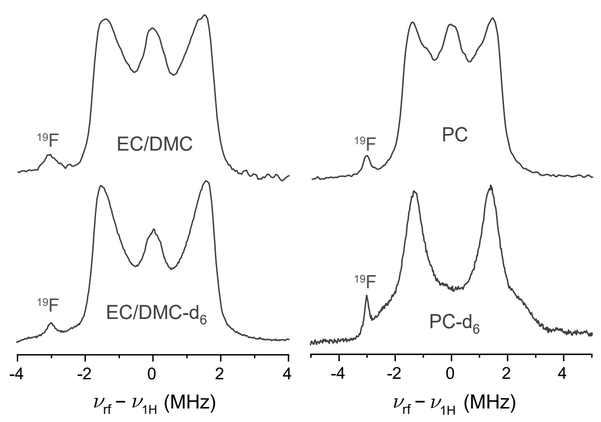
- Transition metal dissolution is a common degradation phenomenon
- for vanadium(V) oxide, vanadyl species are liberated upon the δ- to γ-$Li_xV_2O_5$ phase transition [1]
- EPR detects the vanadyl ions
- the spectrum changes after storing the battery at 45°C for 1 week

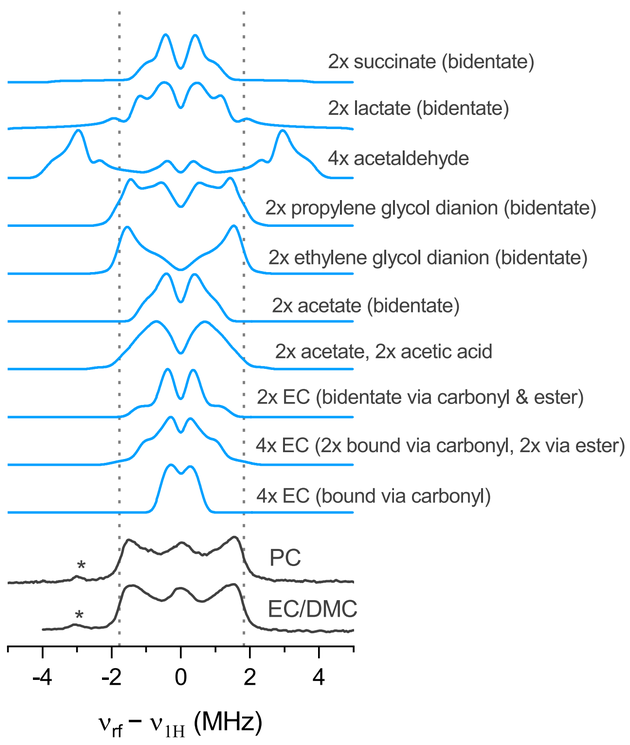


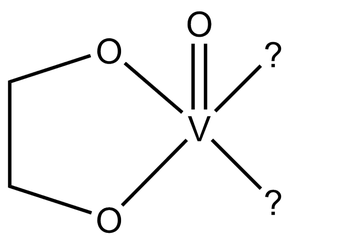
Before heat-treatment



- ENDOR spectra of different electrolyte solutions and deuteration reveals coordination through protons from cyclic carbonates
- the closest fluorine atoms are at a distance of around 6 Å

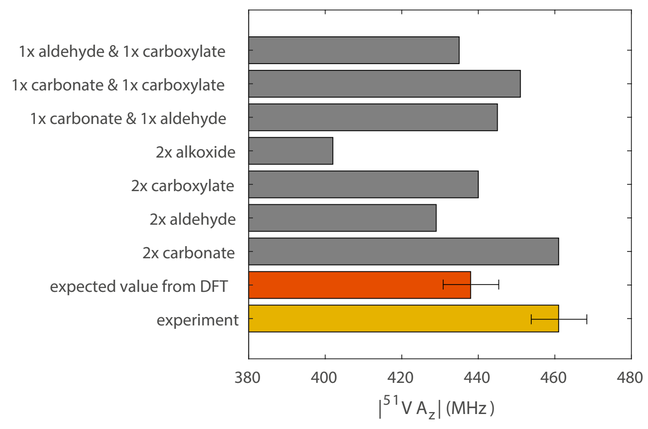






comparing ENDOR traces calculated by DFT, the ethylene (propylene) glycol dianion ligand is identified

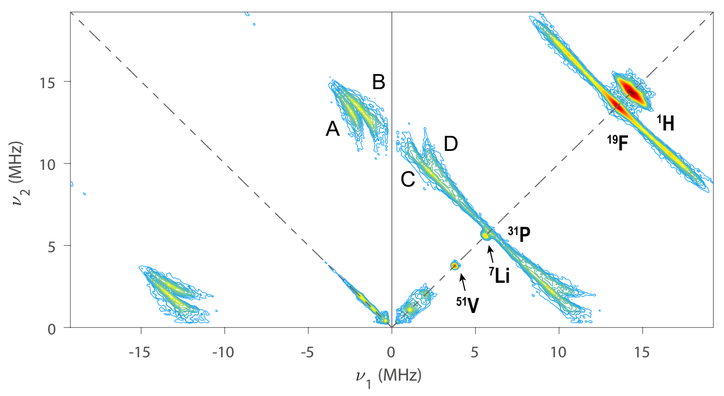
- the identity of the remaining 2 ligands can be estimated by applying the Additivity Rule
- $A_z(^{51}V)$ can be estimated by additive contributions of the chemical group involved in a ligand



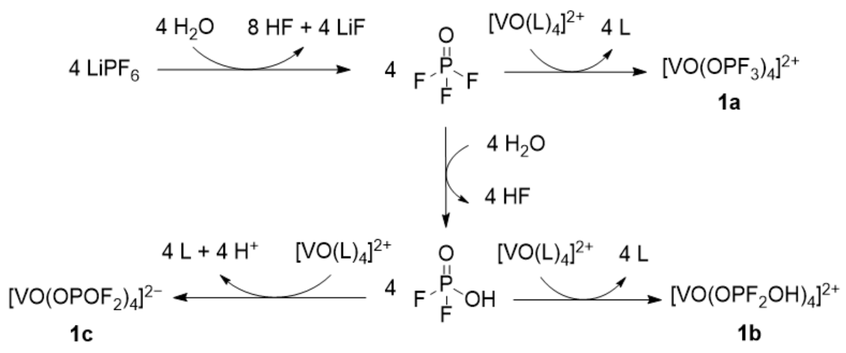
After heat-treatment

$LiPF_6$

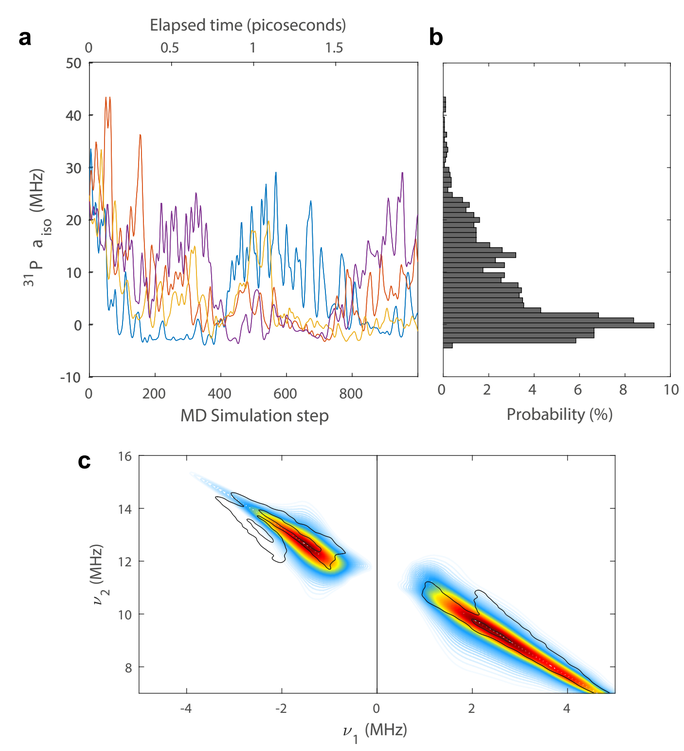
HYSCORE reveals the ligand environment of the vanadyl ion via hyperfine interactions



- the source of phosphorus and fluorine is the electrolyte salt $LiPF_6$
- reaction with trace amounts of water gives phosphoroxy compunds



- phosphoroxy ligands exhibit sensitive changes in hyperfine coupling constants depending on the conformational structure
- bond distances, angles and dihedrals affect isotropic and anisotropic components
- spectra can be reproduced by averaging over a conformational distribution, *e.g.* generated via Molecular Dynamics



References

[1] D. Gourier, A. Tranchant, N. Baffier, R. Messina, Electrochim. Acta 1992, 37, 2755–2764.
[2] C. Szczuka, R.-A. Eichel, J. Granwehr, *in preparation* 2021.
[3] C. Szczuka, P. Jakes, R.-A. Eichel, J. Granwehr, Adv. Energy Sustainability Res. 2021, 2100121.