

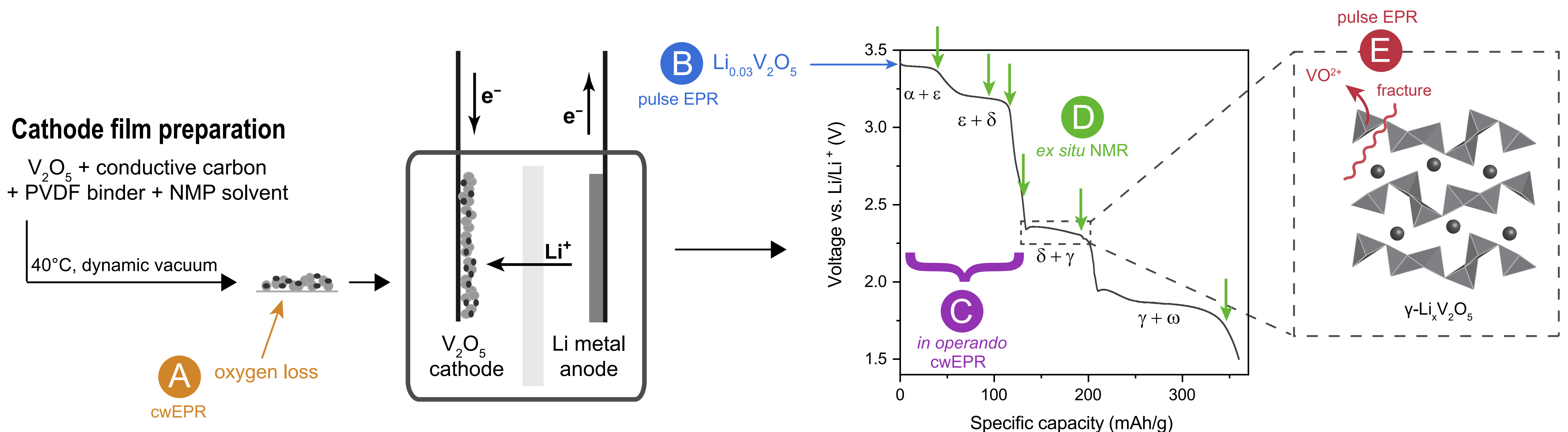
NMR and EPR characterization of V_2O_5 as a cathode material for high-capacity Li-ion batteries

Conrad Szczuka^{a,b}, Peter Jakes^a, Rüdiger-A. Eichel^{a,b} and Josef Granwehr^{a,c}

^aInstitute of Energy and Climate Research (IEK-9), Forschungszentrum Jülich, Jülich, Germany

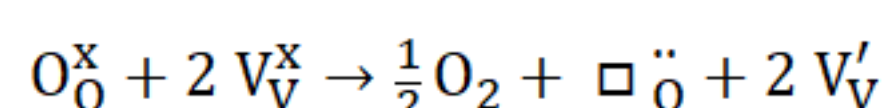
^bInstitute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

^cInstitute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany

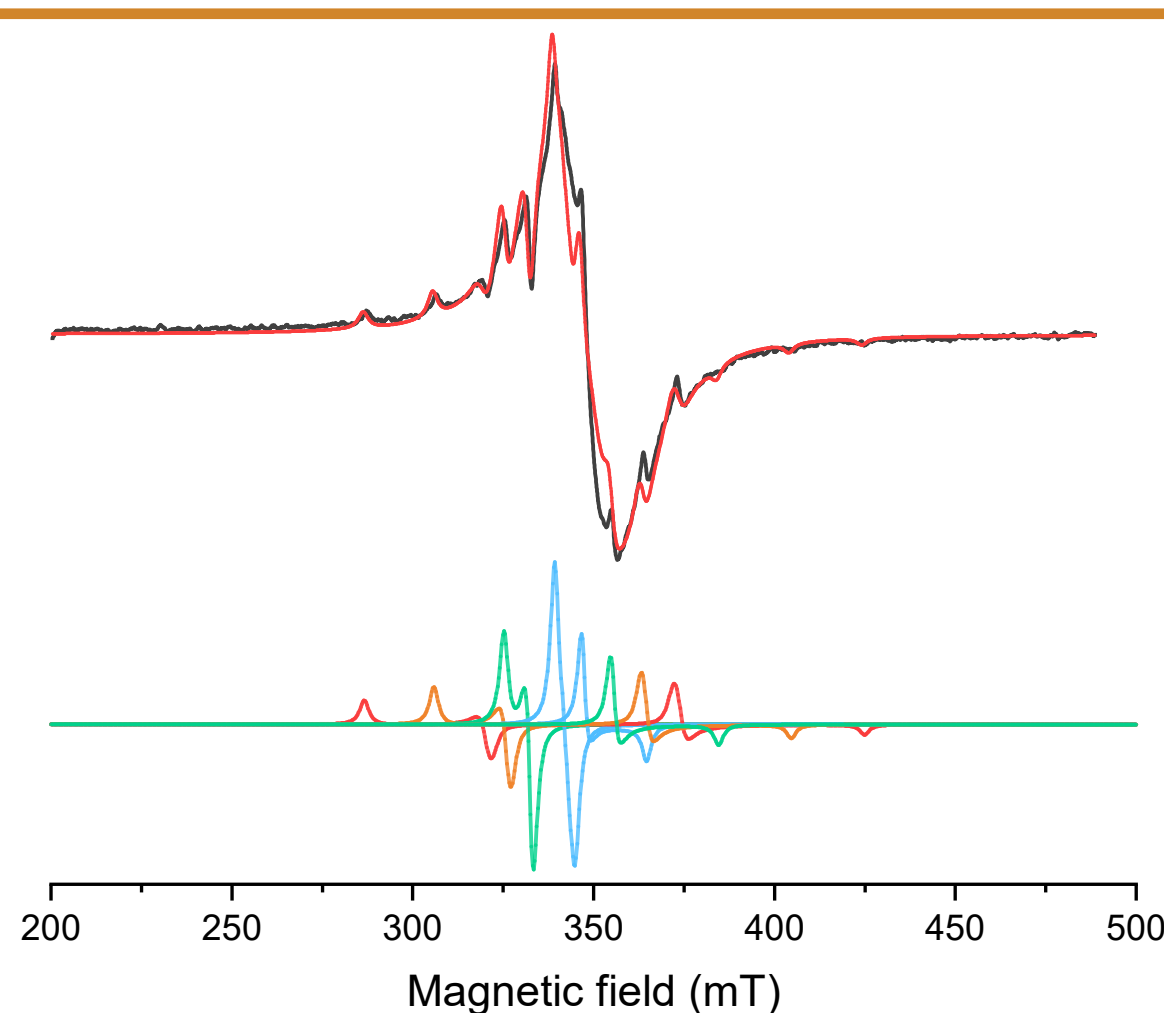


A Defects through oxygen loss

- the drying process causes stoichiometric V_2O_5 to degas oxygen



- excess electrons are found close to the oxygen vacancy [1]
- [cluster]/[isolated] = 8/1

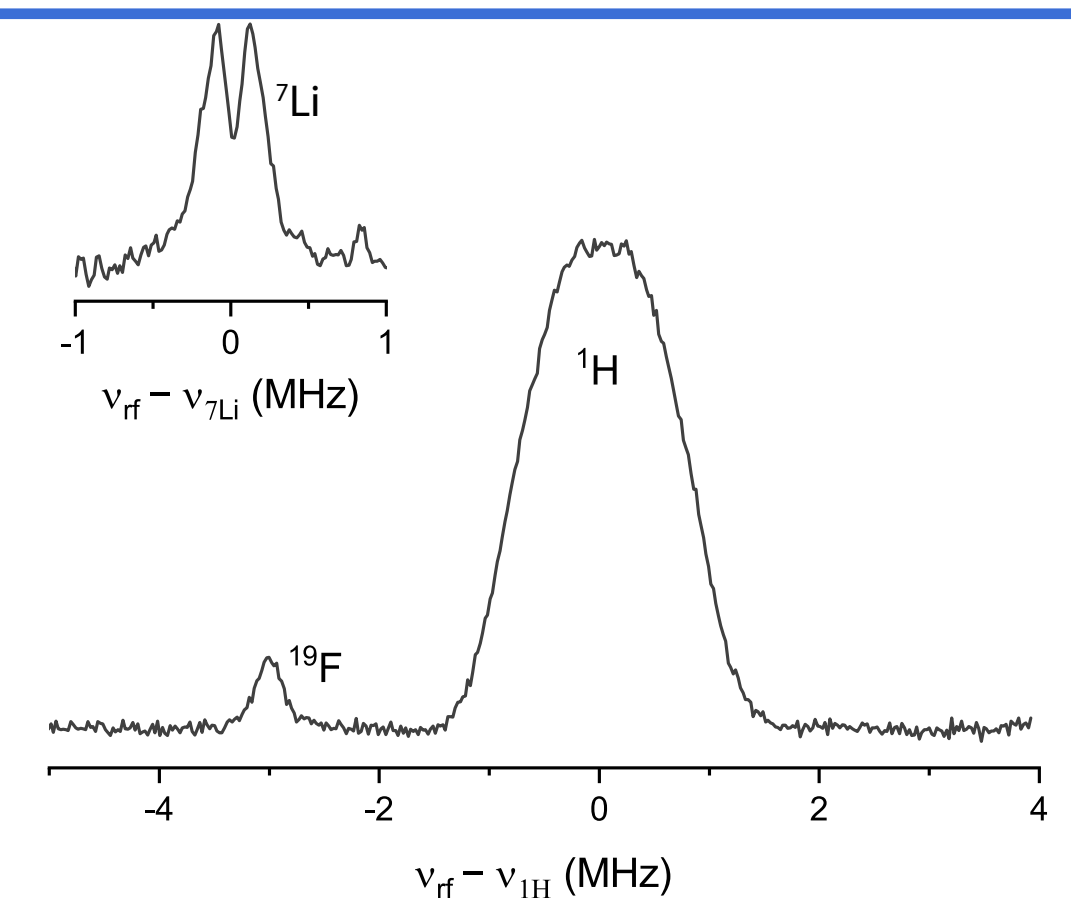


B Initial discharge: $Li_{0.03}V_2O_5$

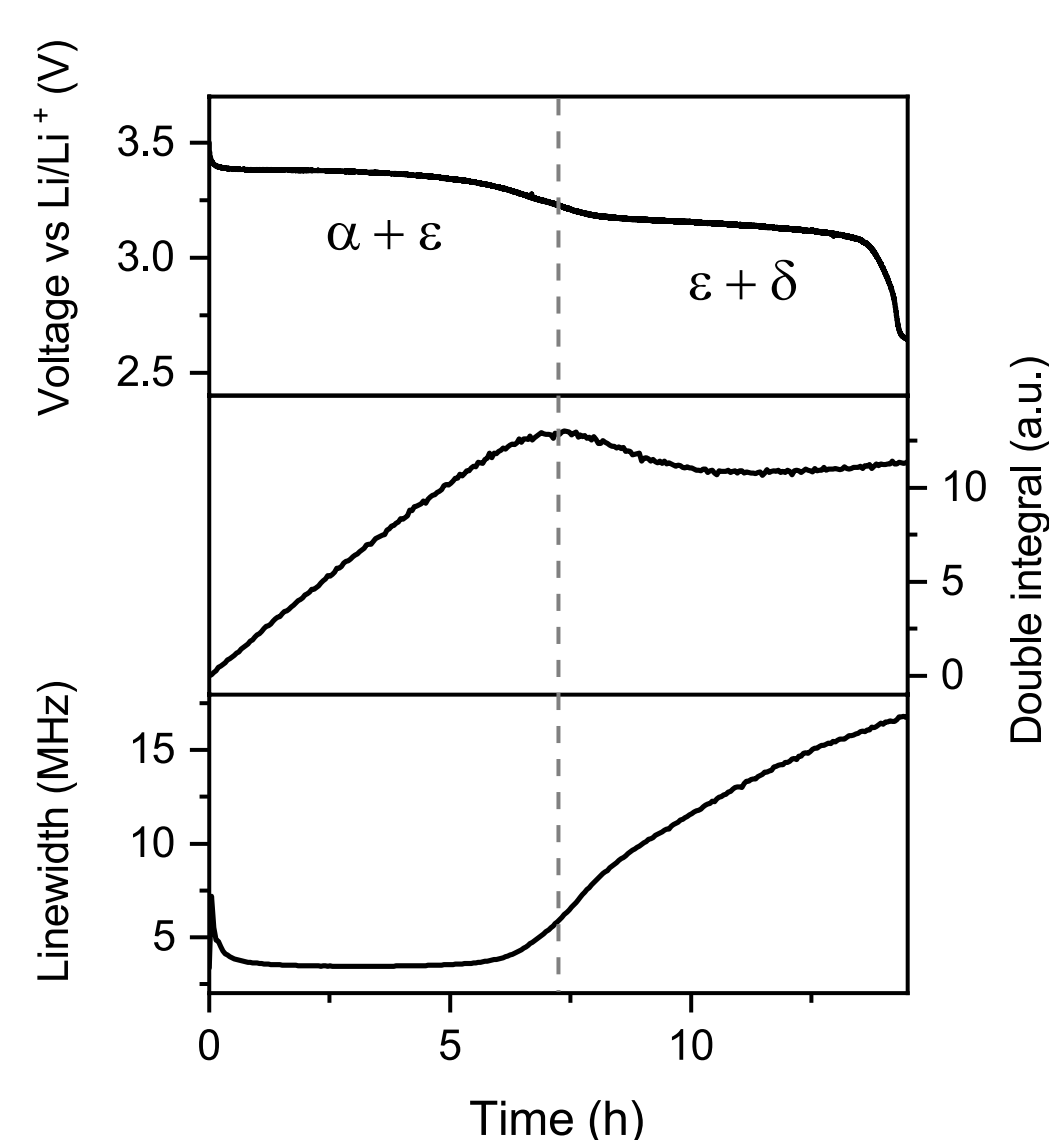
Li reduces the host material with electrons located at V atoms

ENDOR:

coupling to Li, but also strongly to 1H and ^{19}F , suggesting the electrons location to be at the surface



C In operando cwEPR of ϵ and δ phase



With increasing Li concentration:

- (1) Amplitude $\sim \chi$, $M_{x,y}$
- (2) e^-e^- dipolar broadening
- (3) Heisenberg exchange

1st voltage plateau

electron spins are well separated:

- > linear amplitude increase
- > constant linewidth

2nd voltage plateau

broadening and amplitude decrease
e.g. anti-ferromagnetic ordering [2]

D Ex situ MAS NMR

7Li MAS NMR of $Li_xV_2O_5$

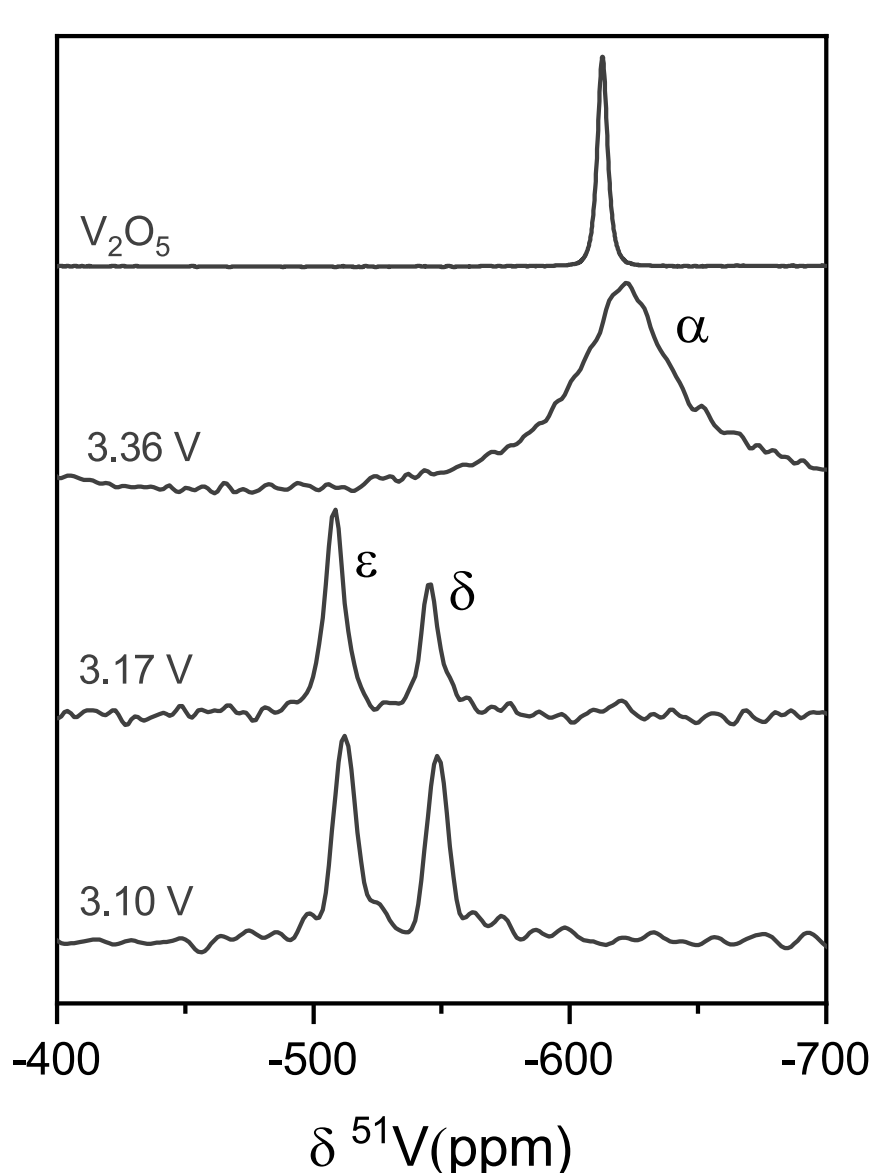
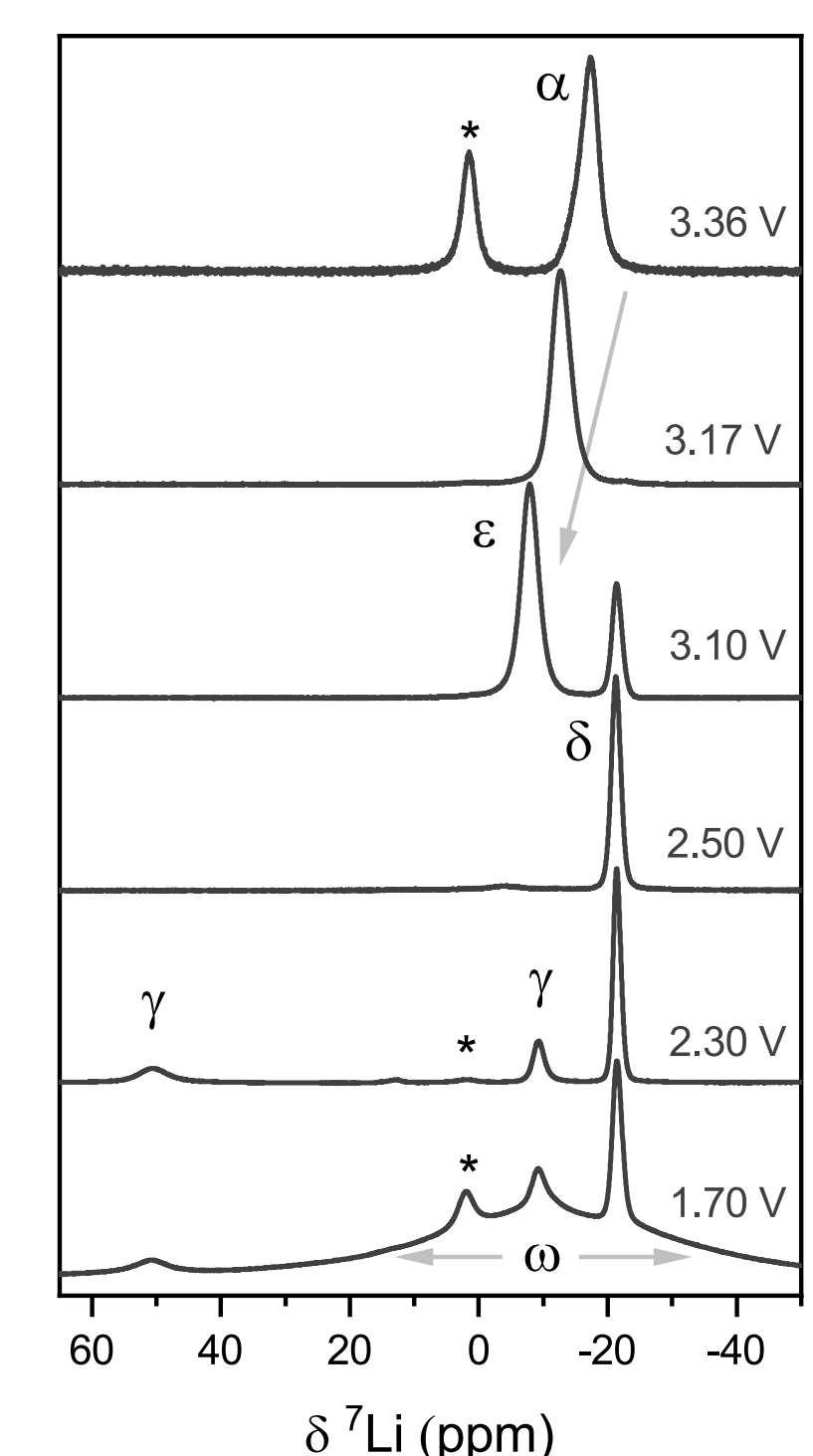
paramagnetic NMR shift
(diamagnetic around 0 ppm, asterisk)

α to ϵ : gradual structure change, in accordance with *in situ* XRD [3]

δ : pure phase around the voltage drop

γ : two signals (chemical exchange via EXSY) albeit one crystallographic site

ω : broad signal indicating severe disorder/amorphous structure



^{51}V MAS NMR of $Li_xV_2O_5$

no drastical change in spinning side-band pattern
-> no severe structural distortion

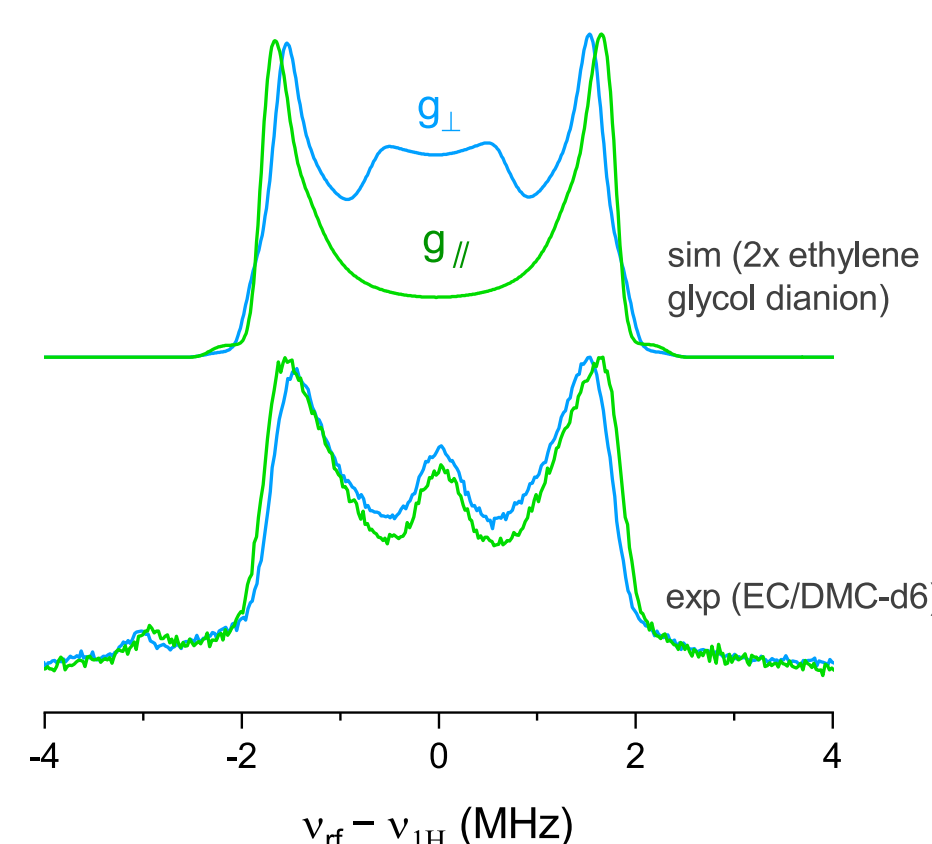
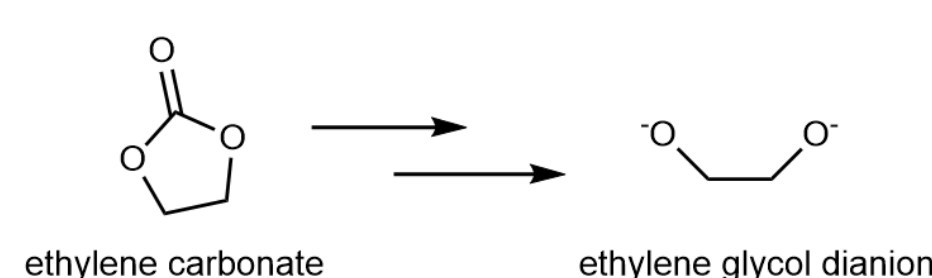
large paramagnetic relaxation (PRE)
-> no signal obtained below 3.0 V

α : resembles pristine V_2O_5 but disordered

ϵ and δ : paramagnetic chemical shift change of around 100 ppm

E Liberated vanadyl species

- upon the δ - to γ - $Li_xV_2O_5$ phase transition, vanadyl species are liberated from the host structure by fracturing [4]
- a few percent of the total V conc. [4]
- ENDOR and DFT:
ethylene glycol dianion as ligand



References

- [1] D. O. Scanlon, A. Walsh, B. J. Morgan, G. W. Watson, J. Phys. Chem. C 2008, 112, 9903–9911.
- [2] P. Pietrzyk, Z. Sojka, Appl. Magn. Reson. 2011, 40, 471–479.

- [3] C. K. Christensen, D. R. Sørensen, J. Hvam, D. B. Ravnsbæk, Chem. Mater. 2019, 31, 512–520.
- [4] D. Gourier, A. Tranchant, N. Baffier, R. Messina, Electrochim. Acta 1992, 37, 2755–2764.