Apport de la RMN du solide à l'étude de matériaux fonctionnels

Un tour d'horizon partiel…

Franck Fayon

Michael Deschamps*, Elodie Salager*, Pierre Florian*, Vincent Sarou-Kanian, Valérie Montouillout, Aydar Rakhmatullin, Catherine Bessada, Dominique Massiot

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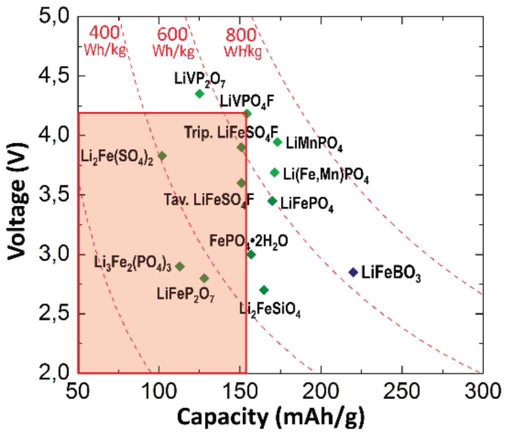
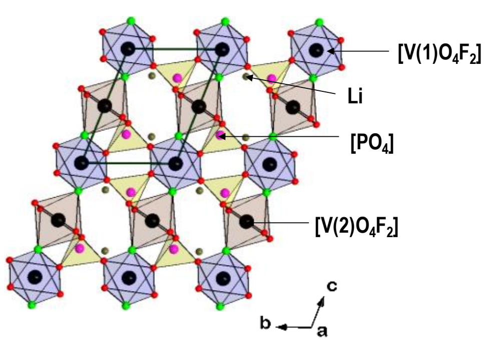
Ultra-fast MAS & high field :
High-resolution ^{7}Li NMR of $LiVPO_4F$, a promising cathode material

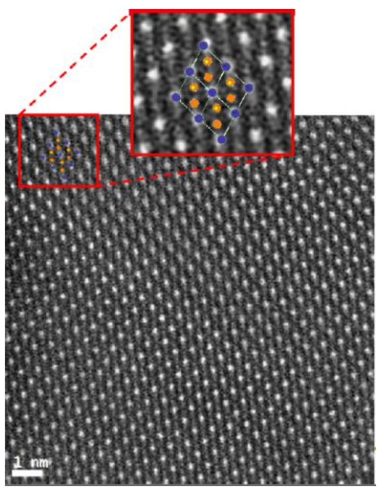
Paramagnetic materials = unpaired electrons = broad lines and short relaxation times !





Masquelier & Croguennec, *Chem. Rev.* **2013**, *113*, 6552–6591

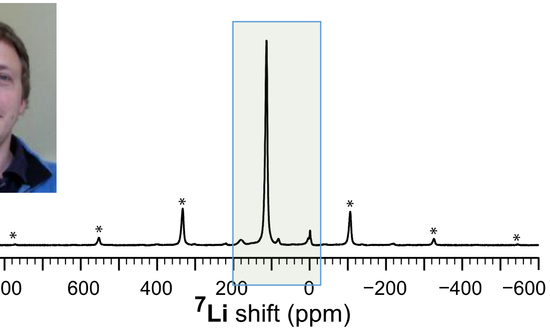
HR-TEM and XRD :
Well-ordered $LiVPO_4F$ crystal structure

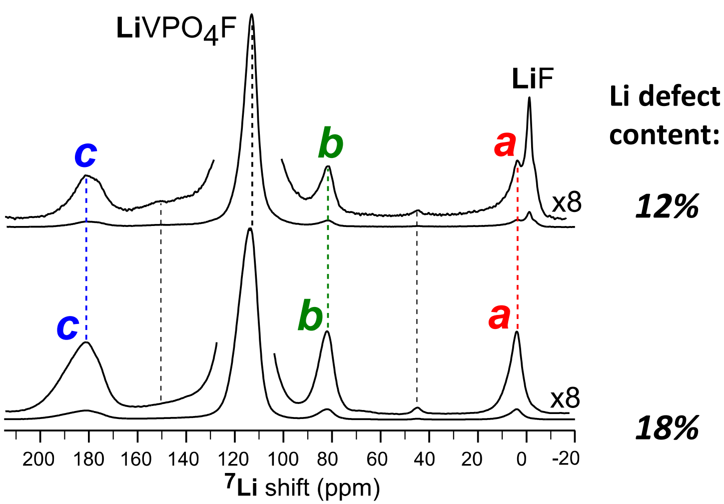


^{7}Li NMR

17.6 T - 750 MHz
64 kHz MAS

M. Deschamps

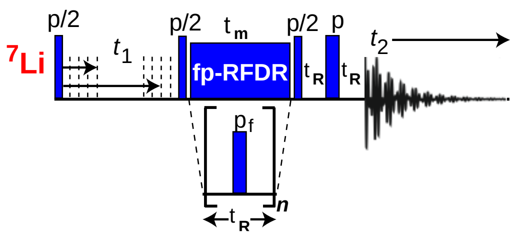




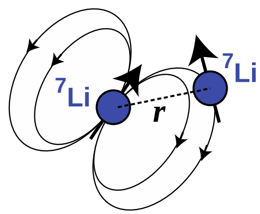
Additional peaks - Impurities or structural defects ?

High-resolution ^{7}Li NMR : Defect or impurities ?
2D HOMCOR to the rescue

^{7}Li NMR



Y. Ishii, *J. Chem. Phys.*, **2001,** *114,* 8473-8483



17.6 T - 750 MHz

64 kHz MAS

Challenge:

T_1's: 7.2 ± 0.8 ms

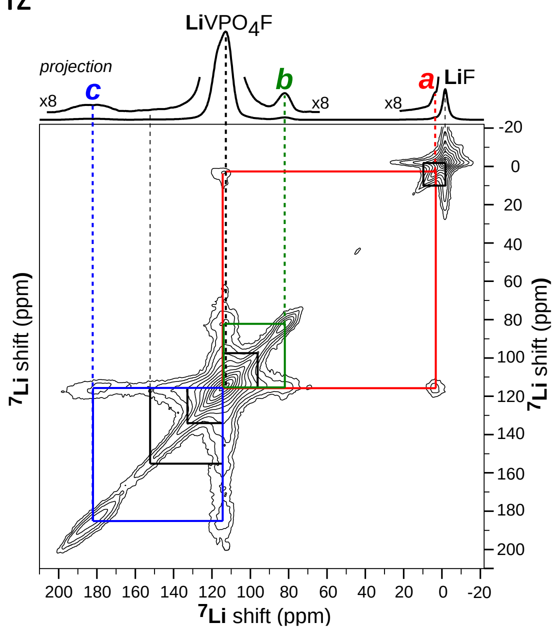
T_2's: 2.0 ± 0.2 ms

10 ms recoupling

50 ms recycling

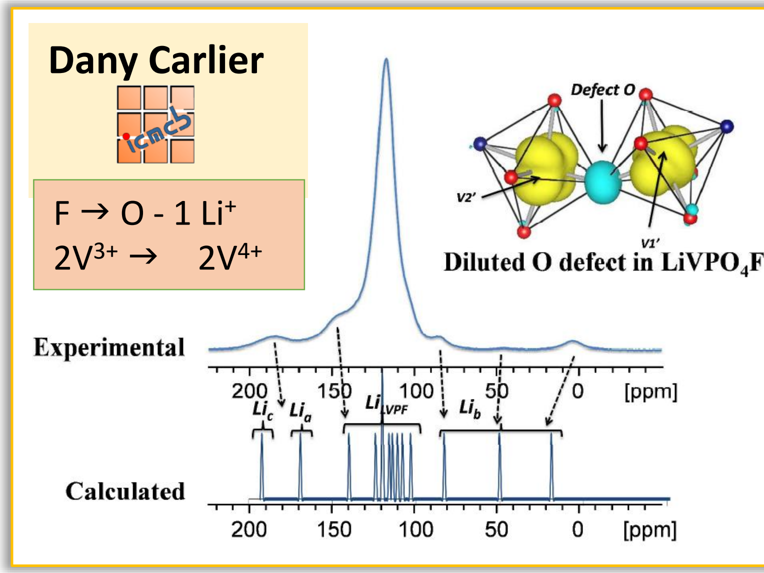
Heating !

T regulation



All peaks belong to the same phase !

DFT computations of ^{7}Li NMR paramagnetic contact shift :



DFT + MAS-NMR explained the *variability* in electrochemistry data

(formation of diluted O structural defects)

R.J. Messinger et al. *Chem. Mater.* 2015, *27(15)*, 5212–5221

E. Boivin, E. et al. *J. Phys. Chem. C* 2016, *120 (46)*, 26187–26198

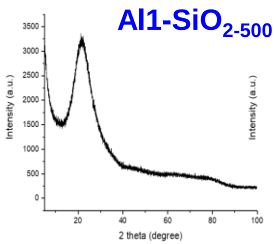
T. Bamine et al. *J. Phys. Chem. C* 2017, *121*, 3219–3227

Atomic-scale structure aluminum oxide layers : ^{27}Al high-field NMR

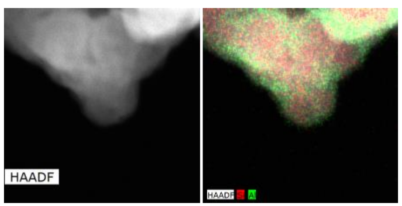
Alumina layers obtained by atomic layer deposition (ALD) of trimethylaluminum onto partially dehydroxylated silica as **heterogeous catalyst**

$SiO_{2\text{-}500}$ —TMA then O_3 (300 °C), 1, 5 or 10 cycles→ $TMA\text{-}SiO_{2\text{-}500}$ —synthetic air (500 °C)→ $Al\text{-}SiO_{2\text{-}500}$

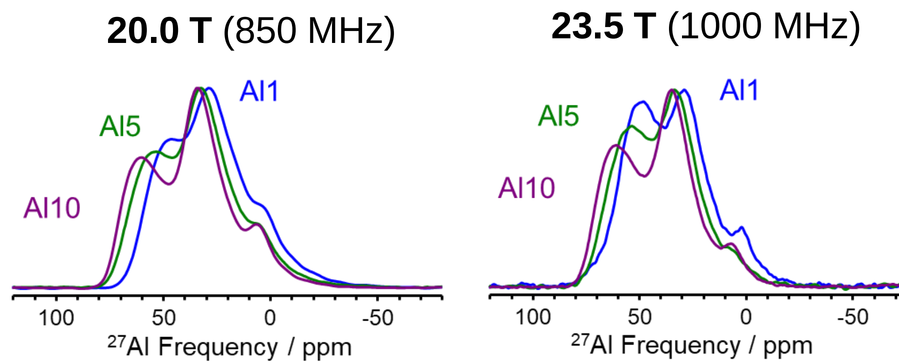
XRD



STEM



^{27}Al very-high field NMR

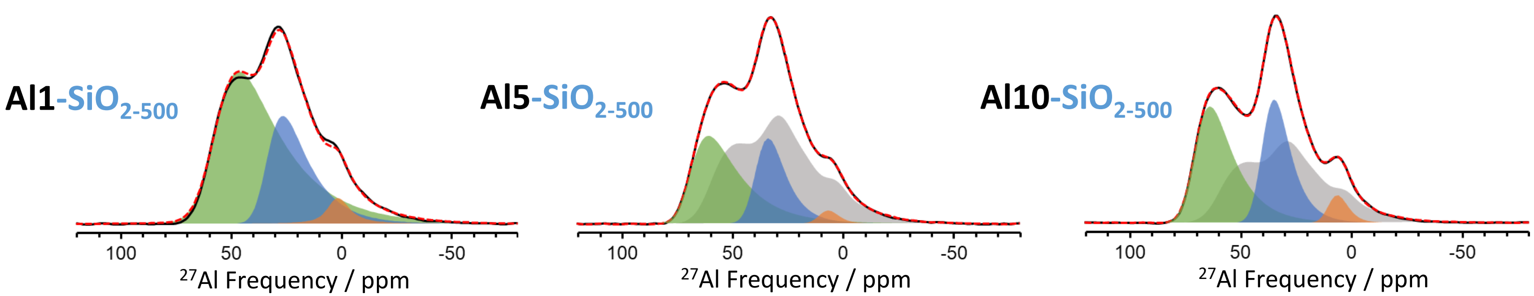


Reducing quadrupolar broadening : Characterization and quantification

Formation of an aluminosilicate sub-monolayer during the first ALD cycle…

… Presence of unaltered $Al1\text{-}SiO_{2\text{-}500}$ layer (completed up to 51% of Al…)

…growth of an "amorphous-Al_2O_3 like" layer



M. Kaushik et al., Chem. Mater 33, 3335, 2021.

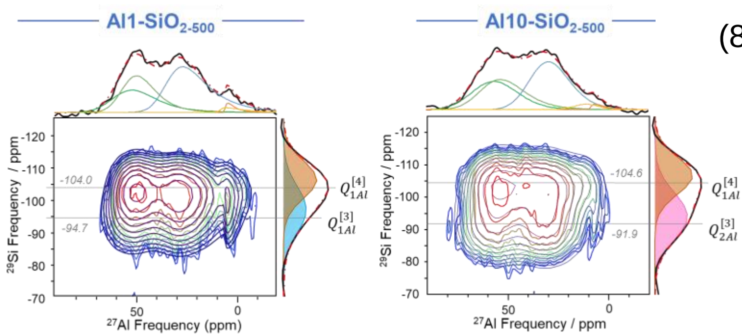
Atomic-scale structure aluminum oxide layers : ^{27}Al high-field NMR

P. Florian

Probing the SiO_2 / Al_2O_3 interface

^{29}Si/^{27}Al correlations (^{27}Al {^{29}Si} D-HMQC)

20.0 T
(850 MHz)



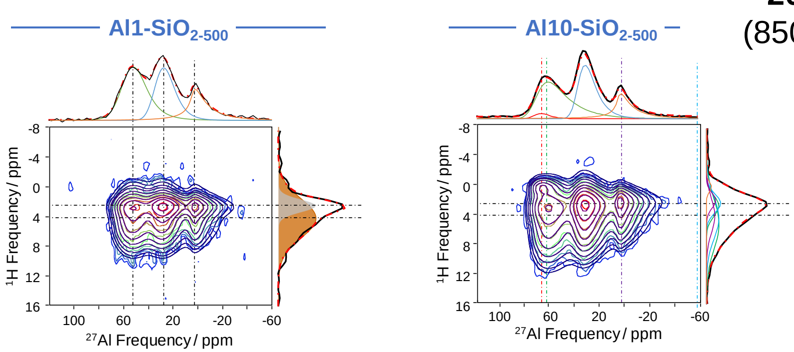
Most likely Al-Si connectivities

Al1 : $^{[4]}Al_{(4Si)}$ - $Q^{[4]}_{1Al}$ and $^{[4]}Al_{(3Si)}$ - $Q^{[3]}_{1Al}$ Al10 : $^{[4]}Al_{(3Si)}$ - $Q^{[4]}_{1Al}$ and $^{[4]}Al_{(2Si)}$ - $Q^{[3]}_{2Al}$

Probing the location of OH groups

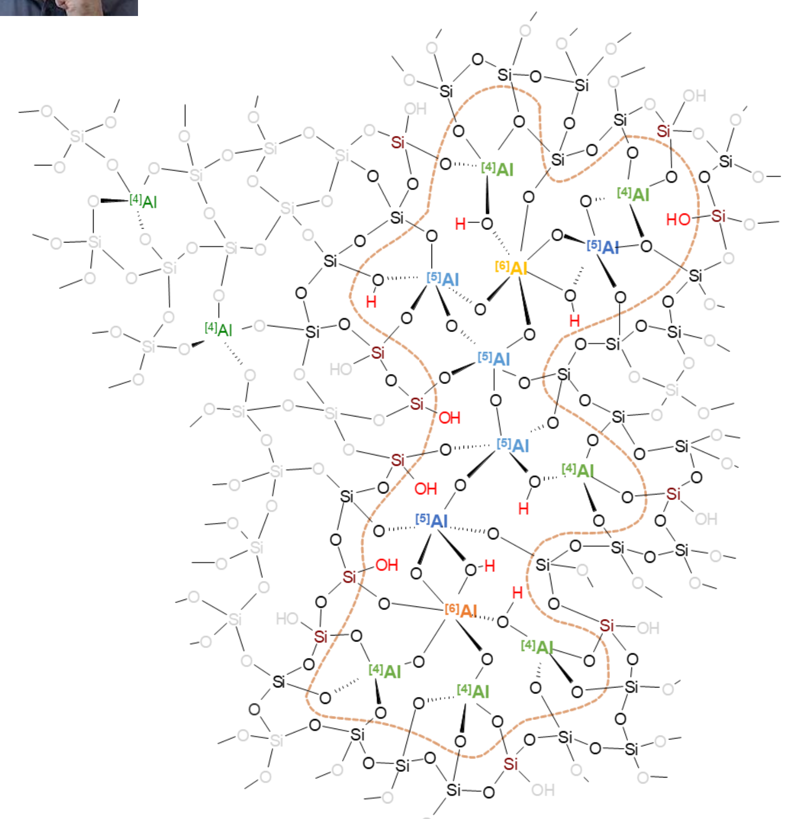
^{1}H/^{27}Al correlations (^{27}Al {^{1}H} D-HMQC)

20.0 T
(850 MHz)



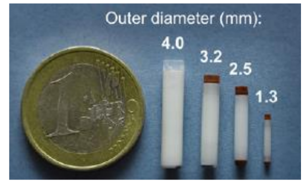
Al oxide layer : ~ 80% Al sites are close to **–OH groups**
Terminal $^{[4]}$**Al(OH)** aluminols signals at the surface of am-Al_2O_3 (not in sub-layer)

Sketch of atomic structure



M. Kaushik et al., Chem. Mater 33, 3335, 2021.

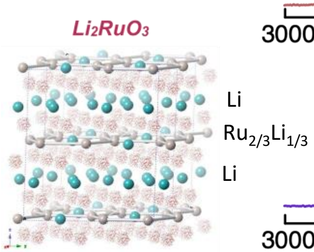
Ultra-fast MAS and beyong :
Increasing spectral resolution and coherence lifetimes

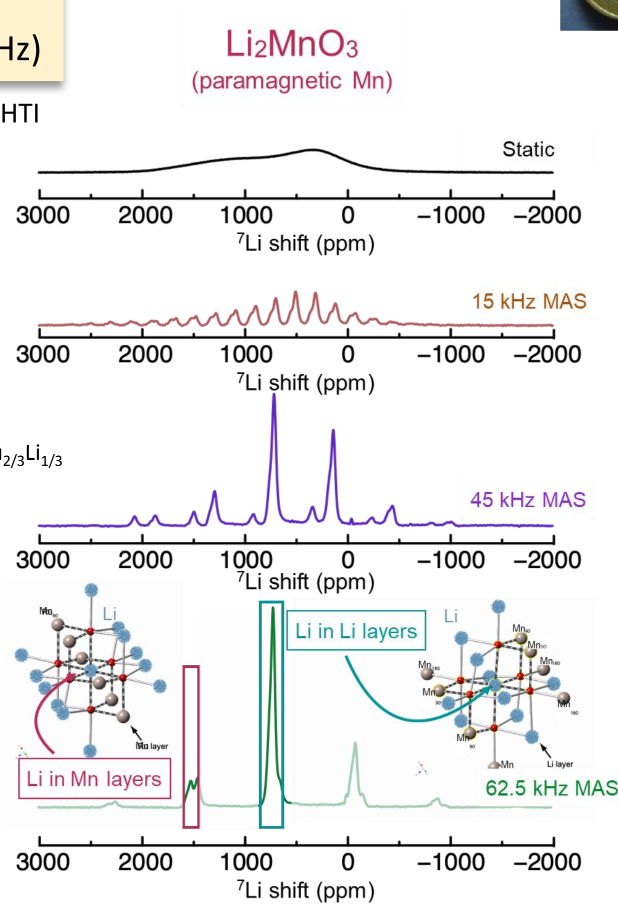


Paramagnetic broadening

^{7}Li NMR
4.7 T (200 MHz)

E. Salager@CEMHTI





ENERGY RS2E

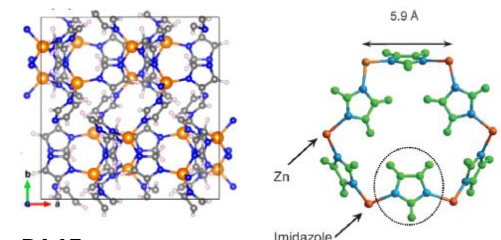
Resolution of the 2 Li sites at fast MAS

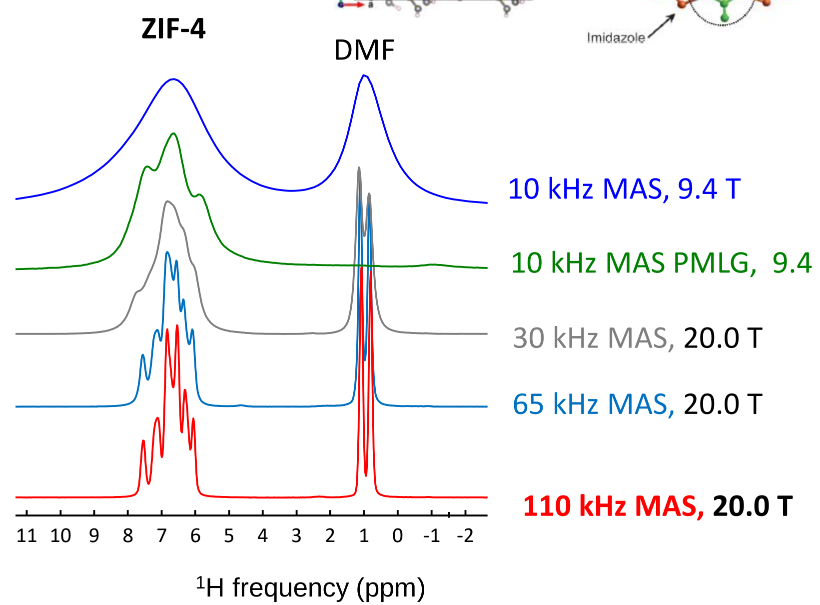
Strong ^{1}H dipolar couplings

^{1}H NMR
20.0 T (850 MHz)

P. Florian@CEMHTI

MOF **"ZIF-4"**
$Zn(Im)_2$





Approaching the resolution of all proton peaks
at **110 kHz MAS** !

Increasing sensitivity – High field DNP NMR

Weakness of NMR is low sensitity

Boltzman → weak population difference between nuclear spin states at room temperature

→ e polarization is much larger : $\gamma e/\gamma^{1}H \sim 660$

→ polarization transfer from unpaired electrons to nuclei

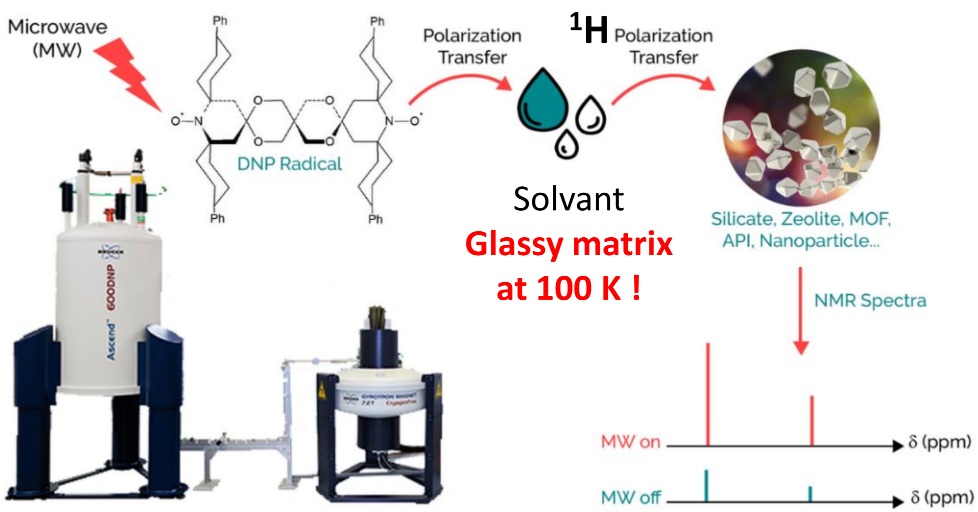
JACS COMMUNICATIONS **2010 !**

Published on Web 09/10/2010

Surface Enhanced NMR Spectroscopy by Dynamic Nuclear Polarization

Anne Lesage,† Moreno Lelli,† David Gajan,‡ Marc A. Caporini,§ Veronika Vitzthum,§ Pascal Miéville,§ Johan Alauzun,‖ Arthur Roussey,‡ Chloé Thieuleux,‡ Ahmad Mehdi,‖ Geoffrey Bodenhausen,§,⊥ Christophe Copéret,‡ and Lyndon Emsley*,†

Sample impregnation



Courtesy of C. Martineau-Corcos

Sensitivity gain > 100-200
Time saving up to 10^5

Surface species
Low concentration
Allows NMR exp. that cannot be done…

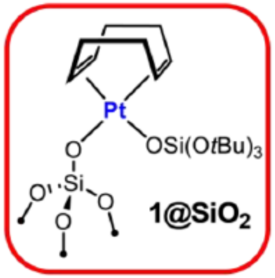
Increasing sensitivity – High field DNP NMR

DNP at moderate field (9.4 T)

Signal enhancement up to **x100 - x250**

Allow experiments that cannot be done without DNP !

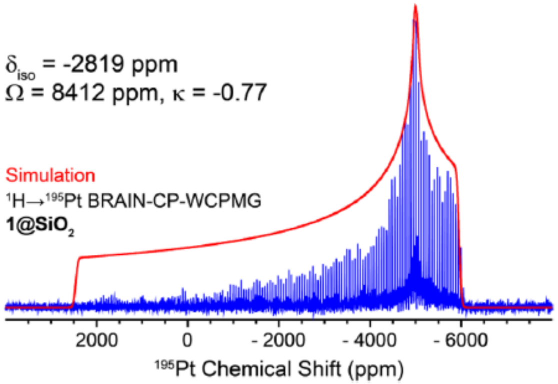
Pt catalyst grafted onto partially dehydrated silica

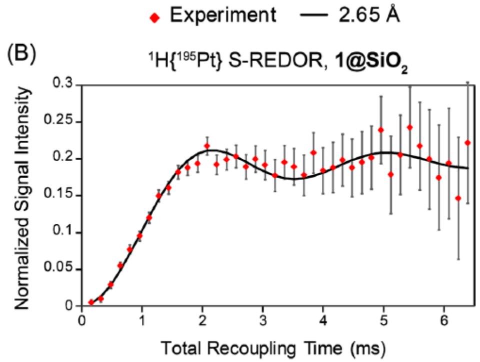


^{195}Pt

ε(^{1}H)~100

^{1}H-^{195}Pt





Alkene ^{1}H – ^{195}Pt

Local structure of grafted species

A. Venkatesh, ….., C. Coperet, A. Lesage, A. Rossini, JACS 142, 18936 (2020)

Current challenge : Very high-field DNP (18.8 – 28.2 T) …… at room temperature

- New radicals, paramagnetic ions, solvent for impregnation
- New microwave sources (pulsed)

Increasing sensitivity : MAS cryo-probe

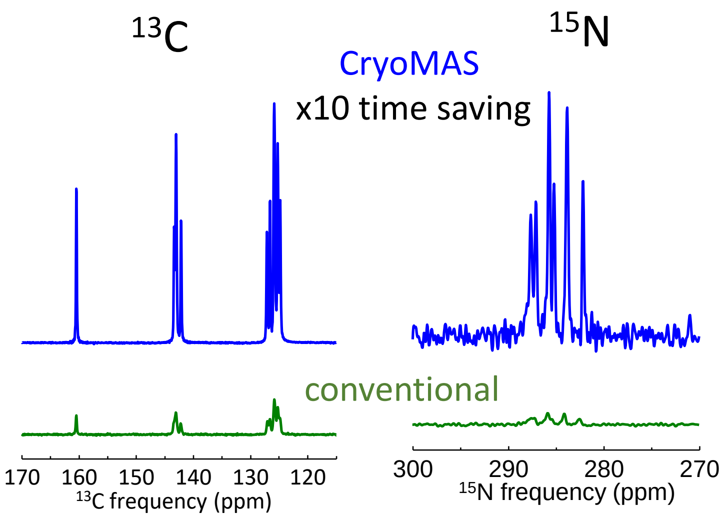
Bruker 2019 innovation

- Cooling the probe coil and preamplifier ~20K (He gas)
- Reducing thermal noise of electronic circuits

- **Increases the sensitivity up to x4**
- **x16 reduction of data collection time**

- **No sample modification**
- **Room temperature**

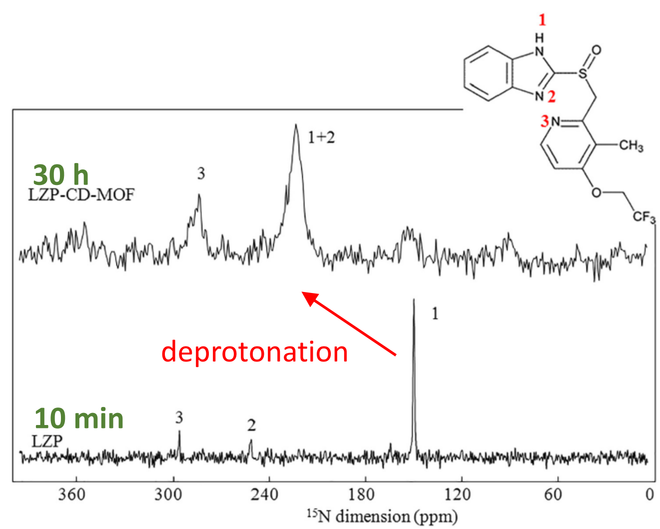
MOF $Zn(Im)_2$ ("ZIF-4")



P. Florian@CEMHTI

Incorporation of lansoprazole in cyclodextrin MOF

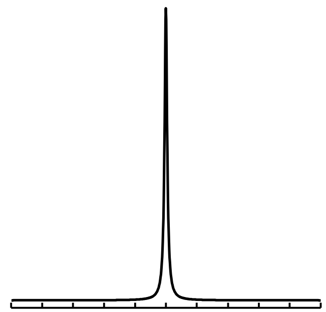
^{15}N at natural abundance, Drug loading ~ 20 %

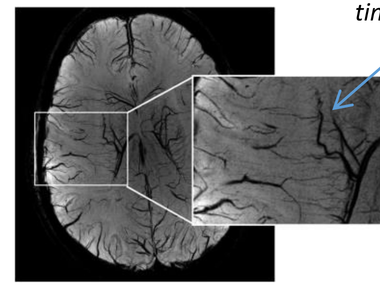


X. Li, M. Porcino, C. Martineau-Corcos, …R. Gref, *Int. J. Pharm.* 585, 119442 (2020).

Perspectives in Magnetic Resonance Imaging of materials

- **A widespread tool for medical imaging of soft tissues**





Res. 0.2x0.2x1.5 mm

susceptibility-weighted image of the brain
tiny venules in the cortex

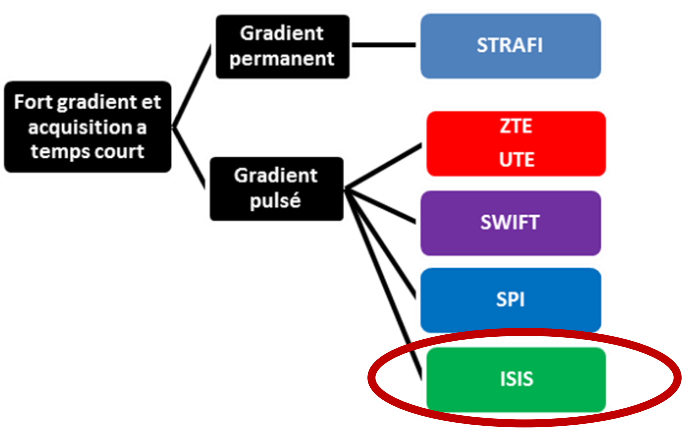
7.0 T

P. Balchandani and T.P. Naidich, Ultra-High-Field MR Neuroimaging, 2015

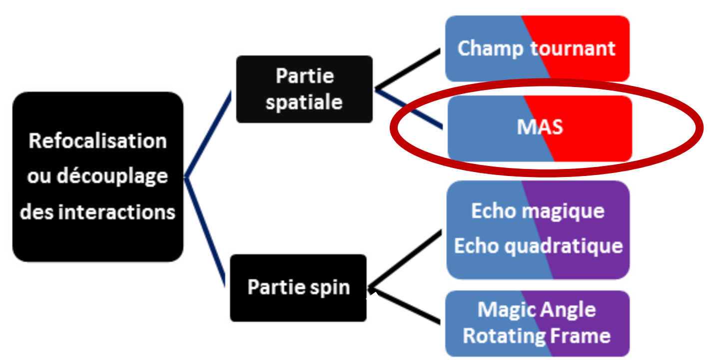
- **Intrinsic difficulties in rigid solids**

Broad lines and usually short transverse relaxation times

Use strong gradients



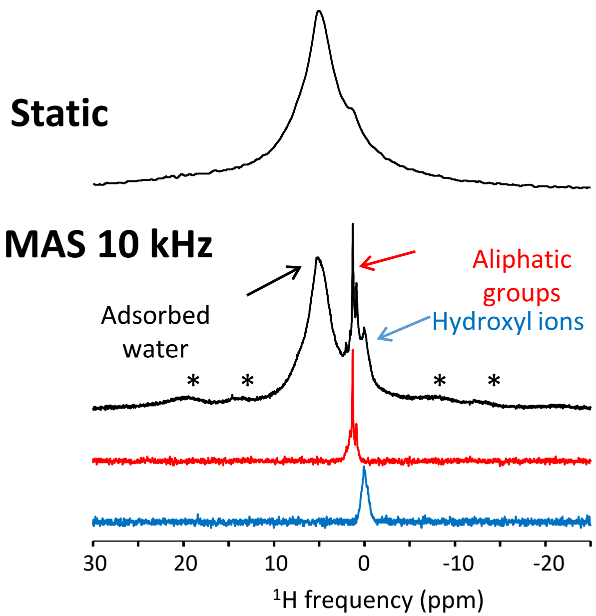
Use averaging methods

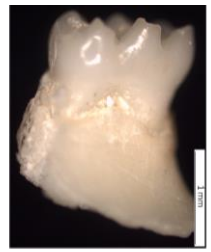


Magic Angle Spinning Magnetic Resonance Imaging

^{1}H 3D spin echo MAS imaging with rotating gradients (synchronized with sample spinning)

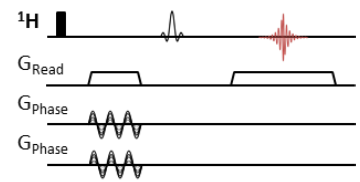
^{1}H (750 MHz)

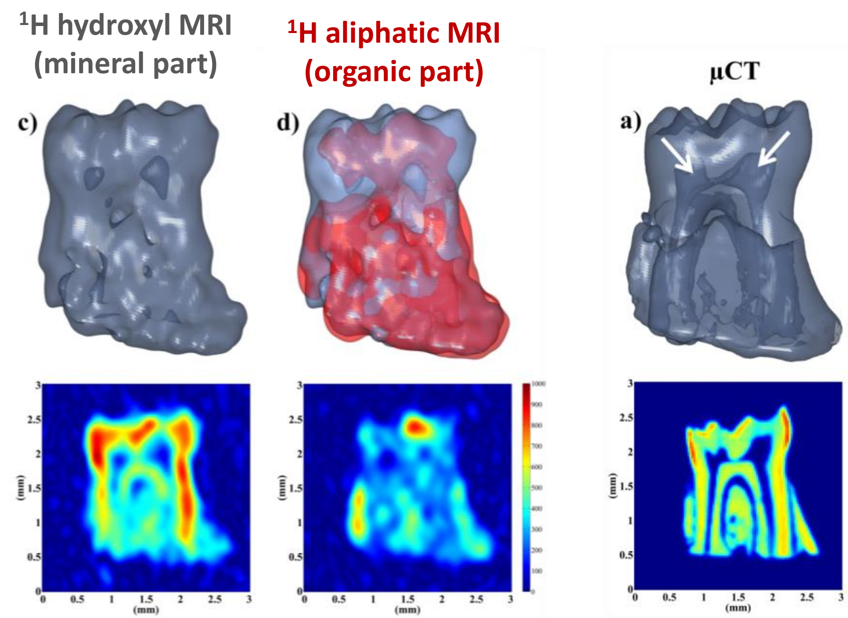




Mouse tooth attached to a piece of bone

^{1}H MAS 10 kHz (750 MHz)





200 µm resolution **18 h !** *4 µm resolution*

- ✓ Increased ^{1}H spectral resolution and dephasing time
- ✓ **Selective chemical micro-imaging of ^{1}H**

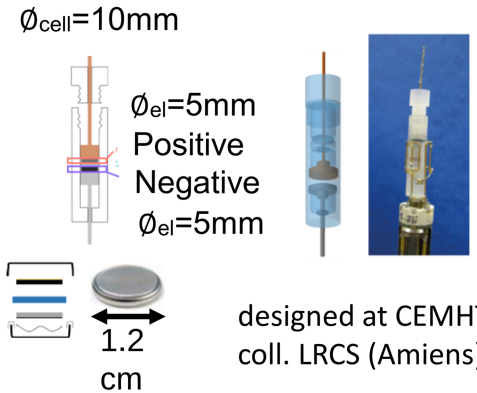
M. Yon et al., *Sci. Rep.* **7,** 8224 (2017)

Electrochemical in situ NMR spectroscopy and imaging

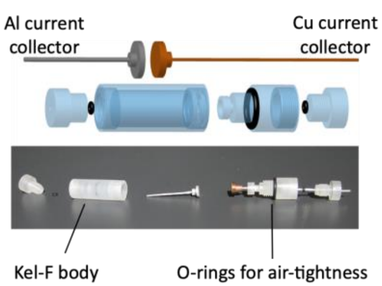
E. Salager

In-situ/operando & paramagnetic materials : Non-spinning conditions

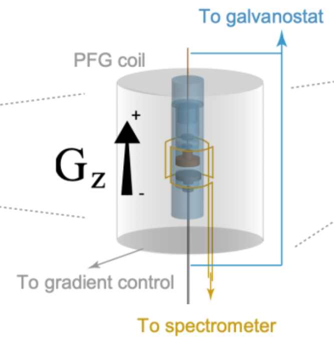
Electrochemical cell designed for NMR



designed at CEMHTI
coll. LRCS (Amiens)



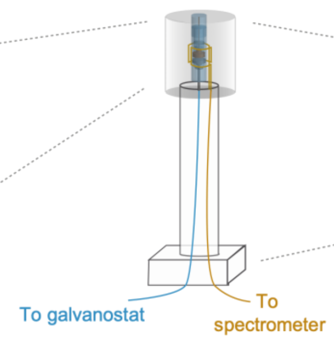
Pulsed field gradient coil



For spatial encoding (imaging)

highest commercially available: **up to 30 T/m**

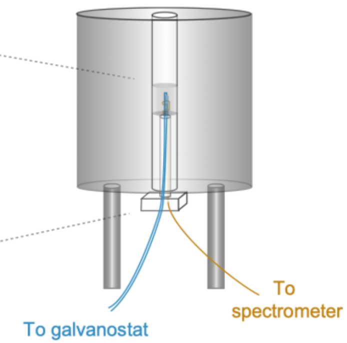
10mm NMR probe



diffusion Bruker probe

For spectroscopy

Wide bore magnet



Bruker **4.7 T, 200 MHz**

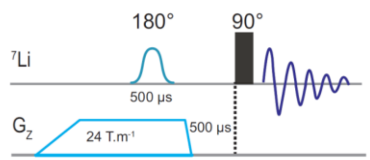
Low field to mitigate paramagnetic effects

Salager et al., Chem. Mater. 2014

Electrochemical in situ NMR spectroscopy and imaging

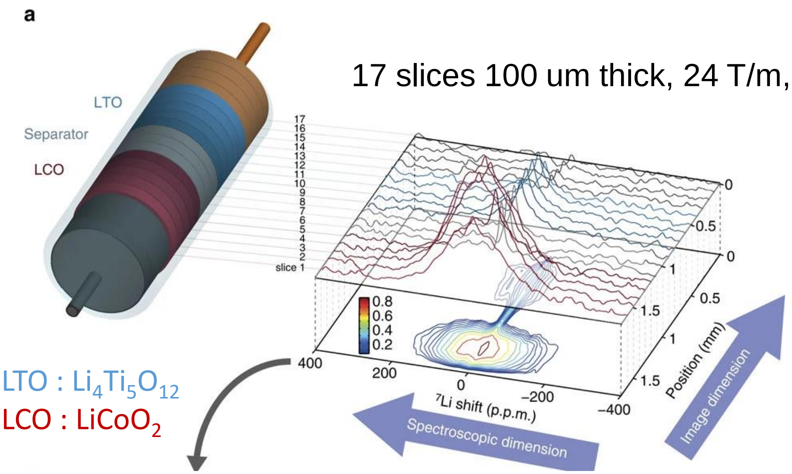
Specific methodology for paramagnetic materials

Image-Selected *In vivo* Spectroscopy

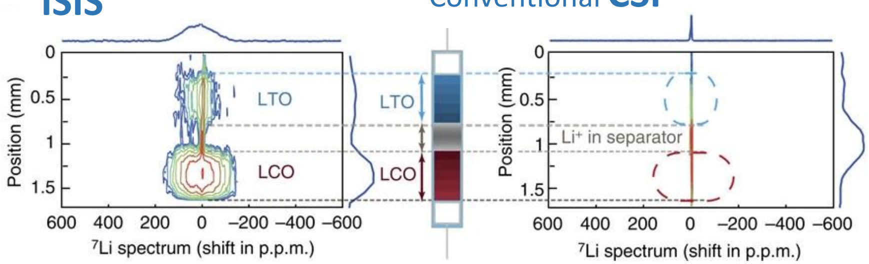


Ultra-short T_2
Longitudinal inversion under gradient

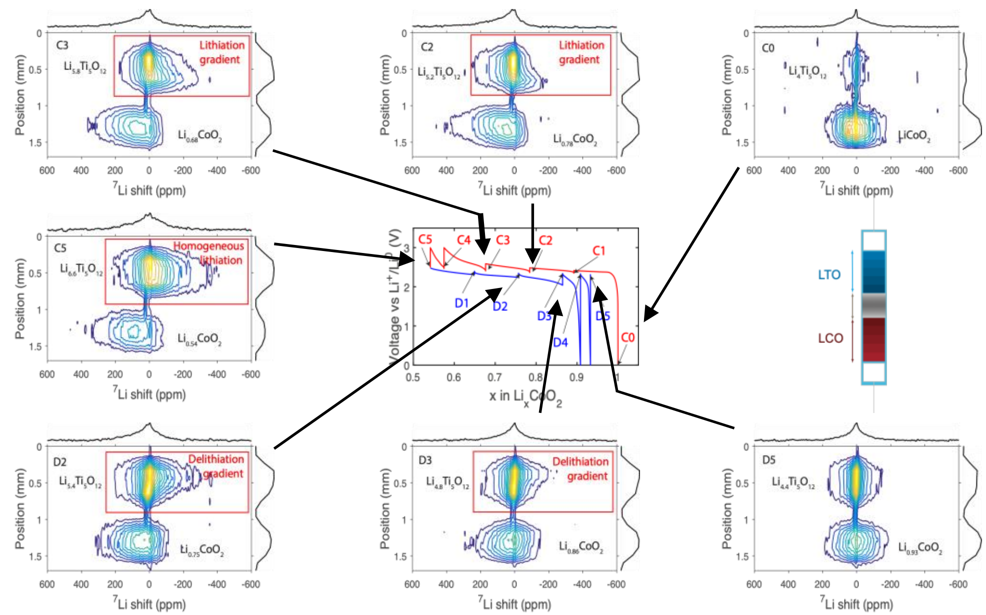
17 slices 100 um thick, 24 T/m, **3h**



LTO : $Li_4Ti_5O_{12}$
LCO : $LiCoO_2$



Following lithiation front during charge and discharge



100 µm spatial resolution

Evidencing :

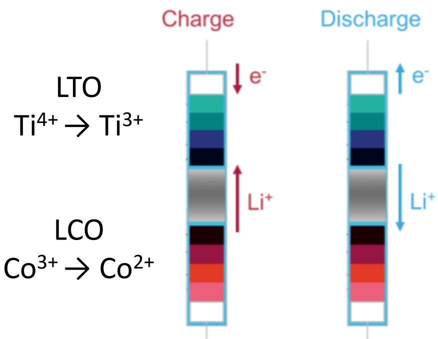
- Lithiation gradient in LTO during charge
- Homogeneous at full charge
- Delithiation gradient in LTO during discharge

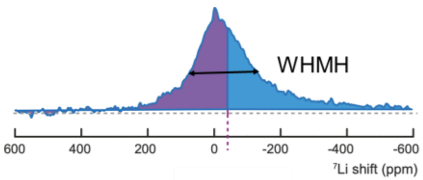
M. Tang et al. Nature Comm. 7, 13284 (2016).

ENERGY RS2E

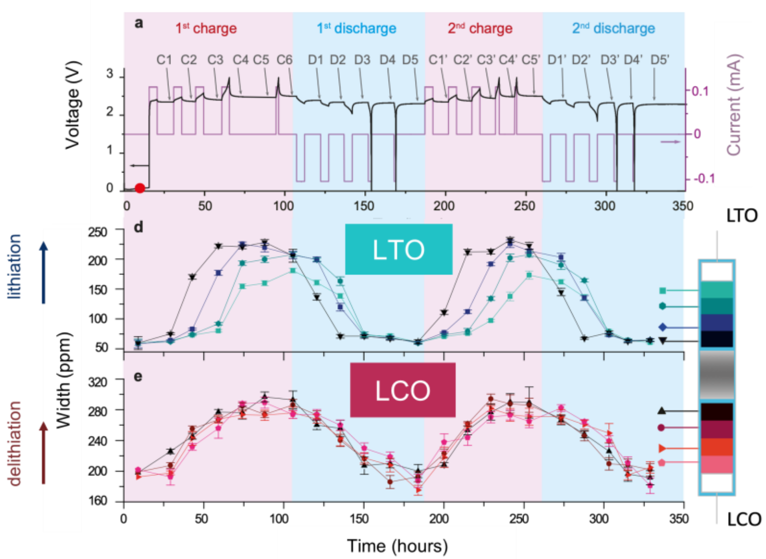
Electrochemical in situ NMR spectroscopy and imaging

Diagnostic for thick electrodes





^{7}Li paramagnetic broadening *vs* charge/discharge

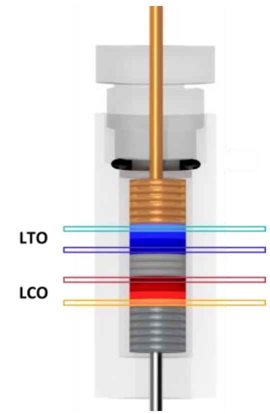


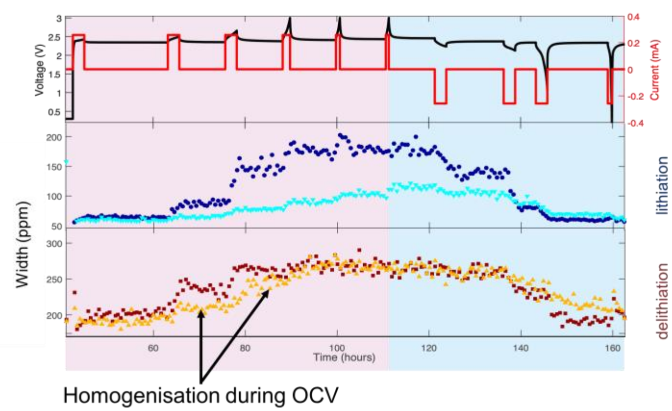
- Lithiation gradient in LTO during charge
- Homogeneous at full charge
- Delithiation gradient in LTO during discharge

Limiting ionic conduction
→ Modify electrode formulation

Improved protocols

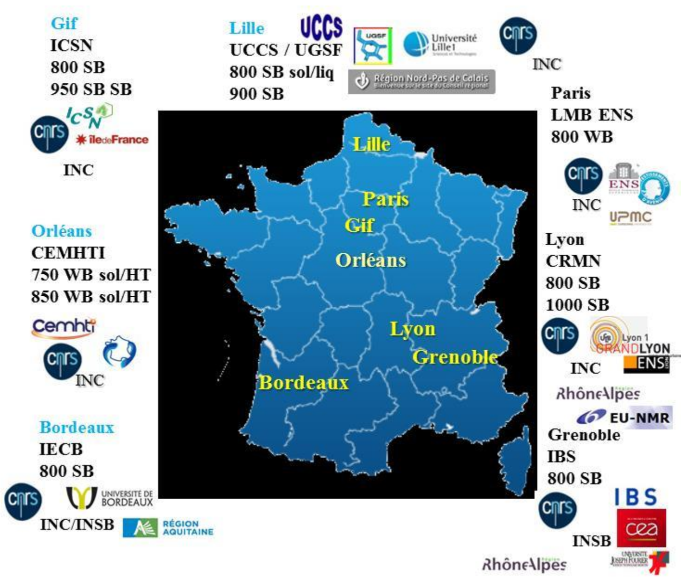
Adapted slice-selection
Faster spectroscopic imaging !
(relaxation phenomena during OCV ?)



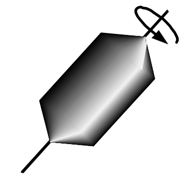


Aging depends on protocol
Pause in open circuit beneficial

M. Tang et al. Nature Comm. 7, 13284 (2016).



1.2 GHz NMR in Lille
juin 2022 !



200 kHz ultra-fast MAS @ 1.0 GHz in Lyon 2022 !

Cryo-MAS @ 850 MHz in Orléans 2023

Merci pour votre attention