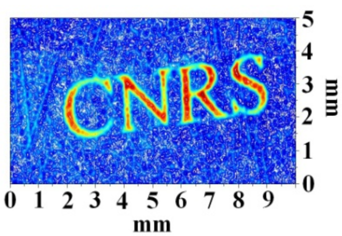
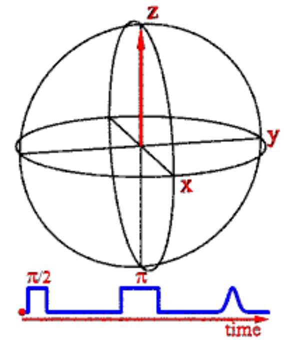
Laboratoire Avancé de Spectroscopie pour les Intéractions, la Réactivité et l'Environnement UMR 8516

Avancées récentes en spectroscopie RPE pour la caractérisation des matériaux

Hervé Vezin





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Workshop CARMEN · EVOLUTION
(21-22 juin 2022, IFPEN, Rueil-Malmaison)

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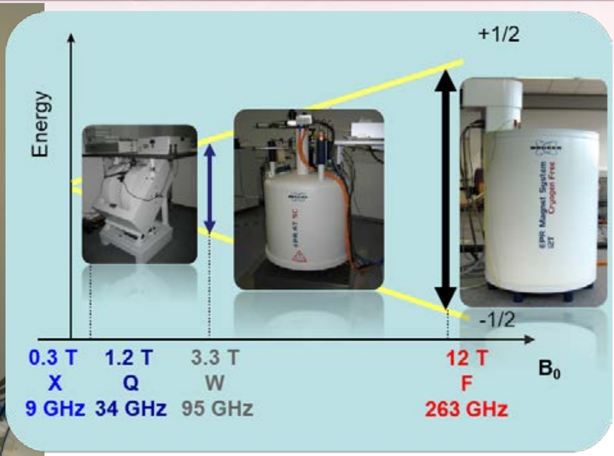
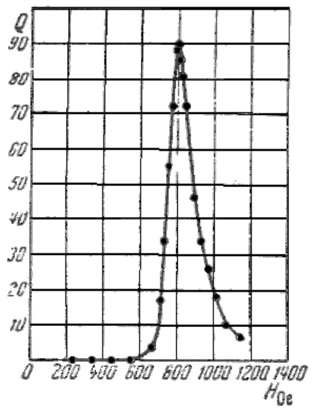
http://lasir.cnrs.fr

A brief history of EPR : 1945-2022

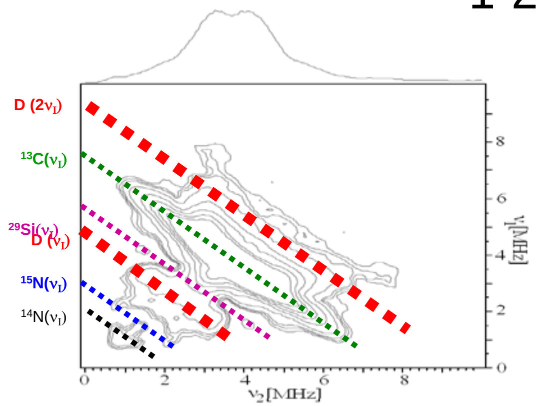


133 MHz

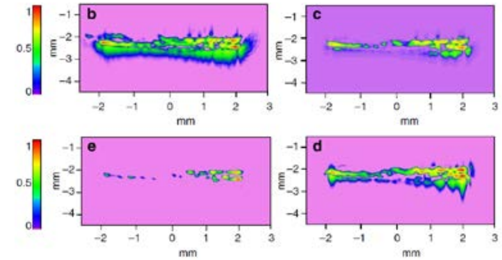


$CuCl_2$

1-263 GHz



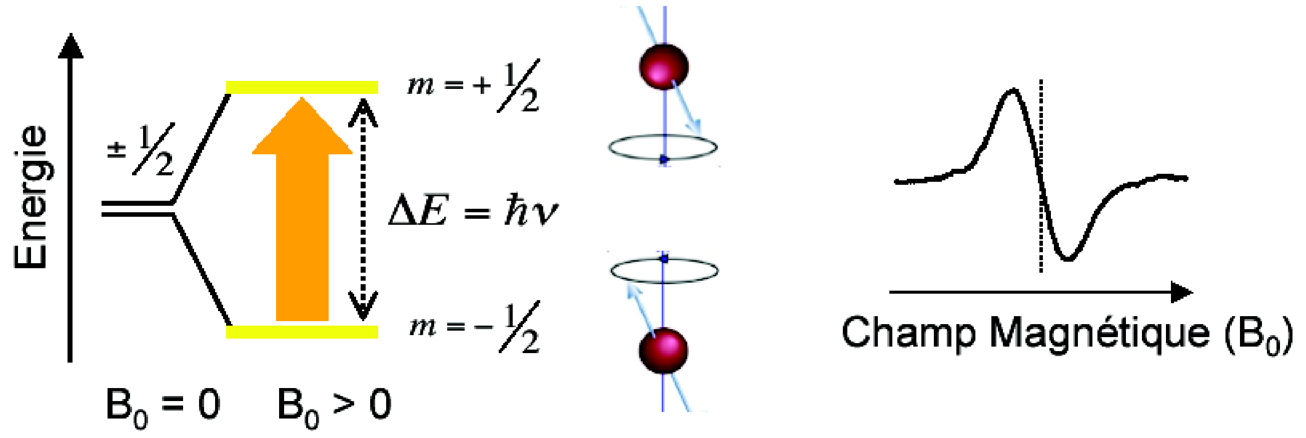
Extraterrestrial organic matter



Battery in operando EPRI

Introduction to EPR spectroscopy

Effet Zeeman



$$\Delta E = \hbar\nu = g\beta B_0$$

- Facteur g: 2,002319304386
- magnéton de Bohr: 9,2740154 10^{-24} J T^{-1}
- champ magnétique: G ou mT
- Cte. de Planck: 6,6260755 10^{-34} J s
- Fréquence: GHz or MHz

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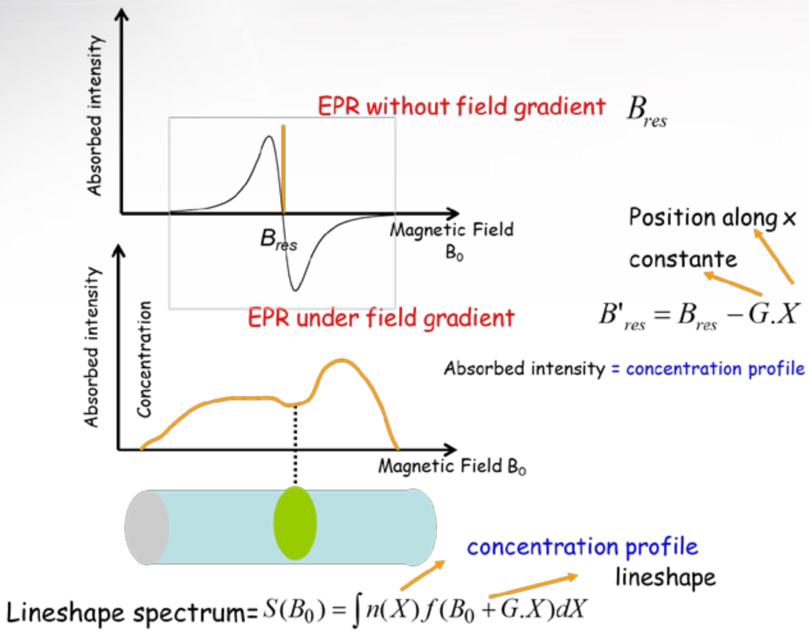
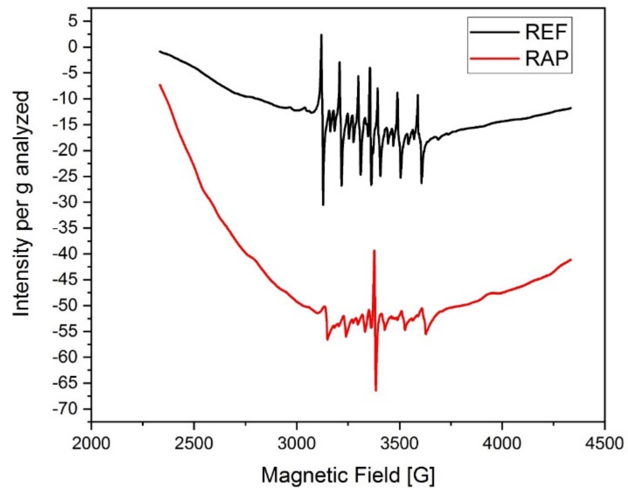
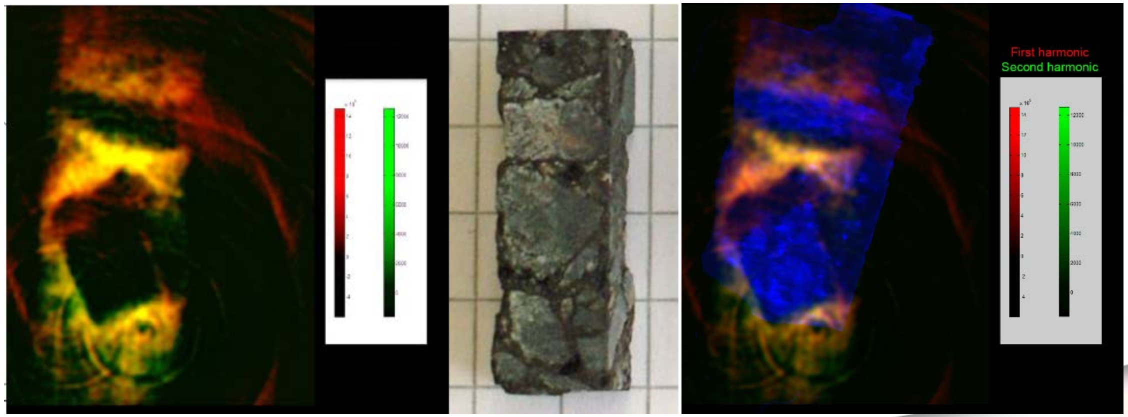
EPR imaging



Absorbed intensity
EPR without field gradient B_{res}
B_{res}
Magnetic Field B_0
Position along x
constante
EPR under field gradient
$B'_{res} = B_{res} - G.X$
Absorbed intensity
Concentration
Absorbed intensity = concentration profile
Magnetic Field B_0
concentration profile
lineshape
Lineshape spectrum= $S(B_0) = \int n(X) f(B_0 + G.X) dX$



REF
RAP
Intensity per g analyzed
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
2000
2500
3000
3500
4000
4500
Magnetic Field [G]



First harmonic
Second harmonic

Mesoporous materials

IN OPERANDO CATALYSIS EPR IMAGING

In-Situ EPR spectroscopy for catalyst

Ethanol transformation into higher hydrocarbons over HZSM-5 zeolite:
Direct detection of radical species by in situ EPR spectroscopy

Physical–chemical characterizations of the fresh and coked HZSM-5(40) zeolite.

Zeolite	%C (wt)	Micropore volume ($cm^3\ g^{-1}$)	Acidity[a] ($\mu mol\ g^{-1}$)		Amount of rad. species ($\mu mol\ g^{-1}$ catalyst)
			Brønsted	Lewis	
Fresh	/	0.177	297	47	/
Coked (0.5 h)	2.2	0.154 (13%)	247 (17%)	34 (28%)	0.94
Coked (1 h)	2.3	0.120 (32%)	241 (20%)	32 (32%)	0.99
Coked (24 h)	6.1	0.081 (54%)	72 (76%)	27 (43%)	4.6

(xx %) = loss.
[a] Number of acid sites able to retain pyridine at 423 K.

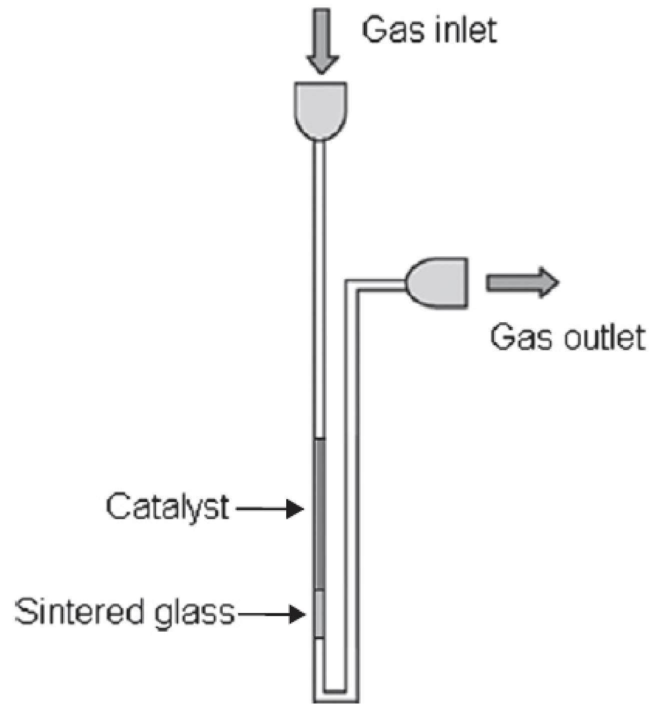


Fig. 1. Cell dedicated to the EPR experiments.

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In-Situ EPR spectroscopy for catalyst

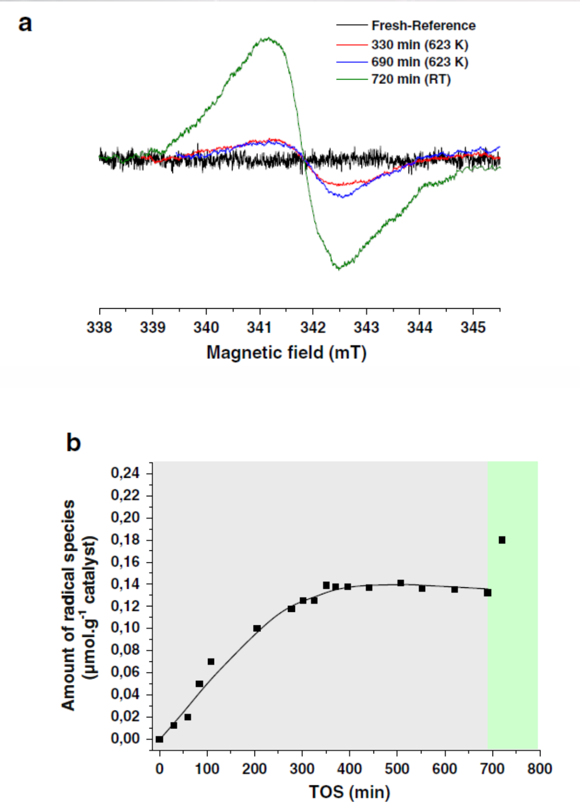


Fig. 4. CW-EPR spectra at various TOS (a) and amount of radical species (b) for the HZSM-5(40) fresh catalyst (from 0 to 720 min).

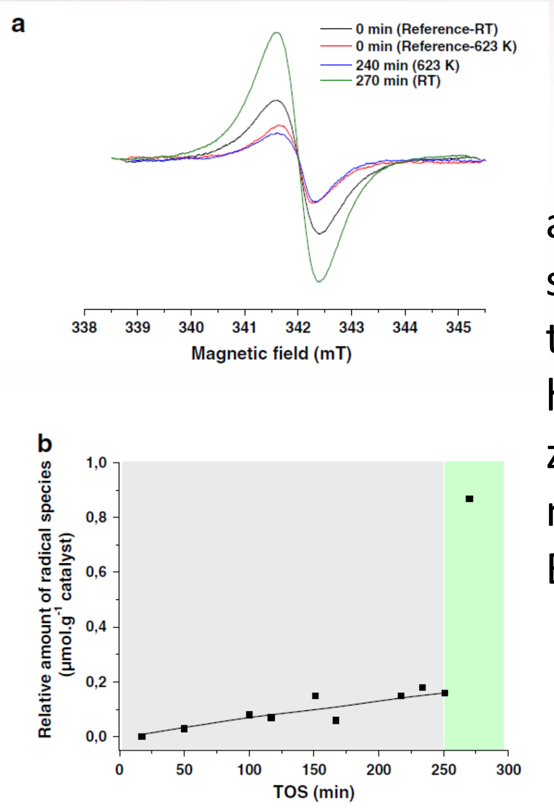


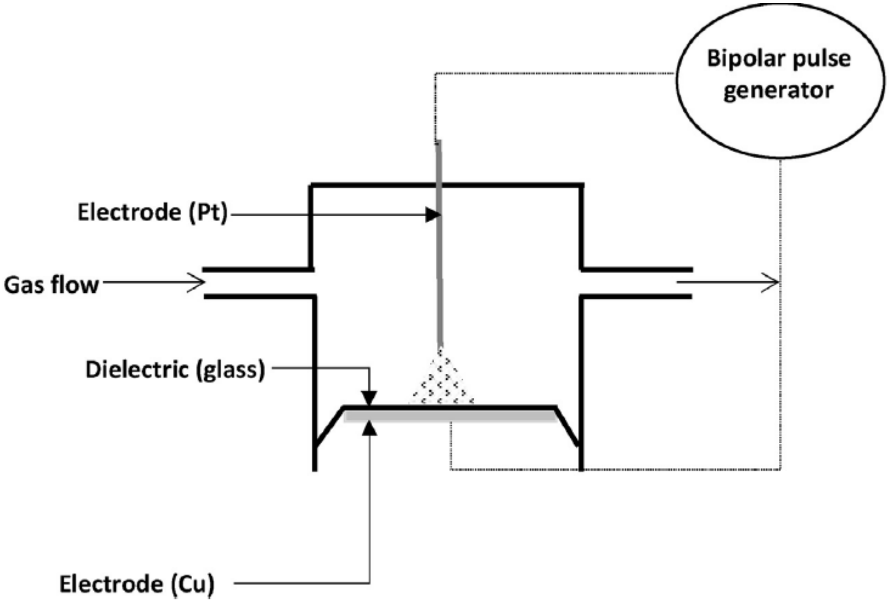
Fig. 5. CW-EPR spectra at various TOS (a) and relative amount of radical species (b) for the HZSM-5(40) coked catalyst (from 0 to 270 min).

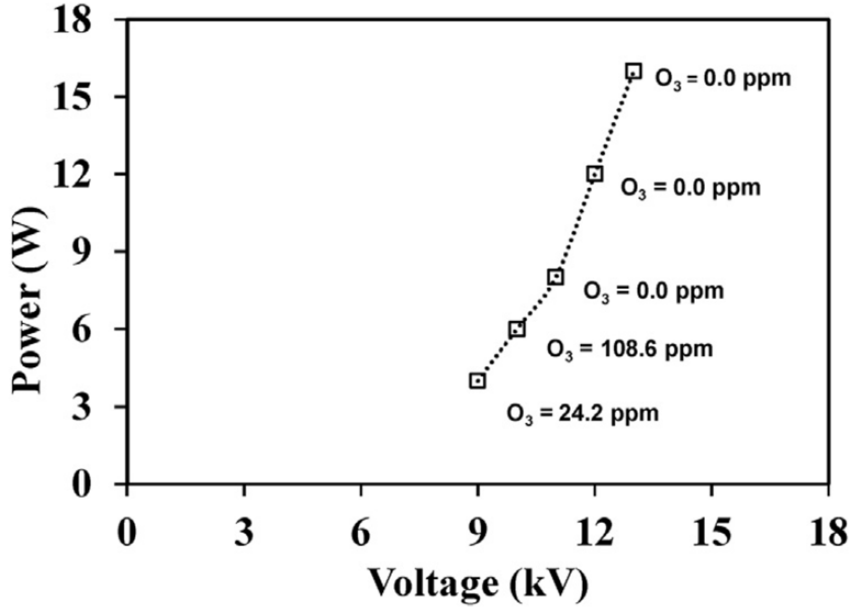
after 24 h of reaction there was still complete ethanol transformation into C_{3+} hydrocarbons over HZSM-5(40) zeolite, even though a 54% loss of microporosity and 76% loss of Brønsted acidity

Ben Tayeb, K. *et al.* Ethanol transformation into higher hydrocarbons over HZSM-5 zeolite: Direct detection of radical species by in situ EPR spectroscopy. *Catal. Commun.* **27**, 119–123 (2012).

New routes for complete regeneration of coked zeolite

Coked zeolite | Fresh zeolite | Zeolite after plasma treatment





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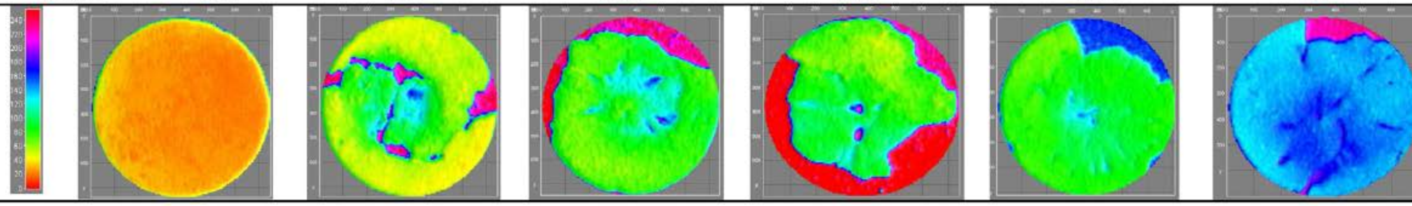
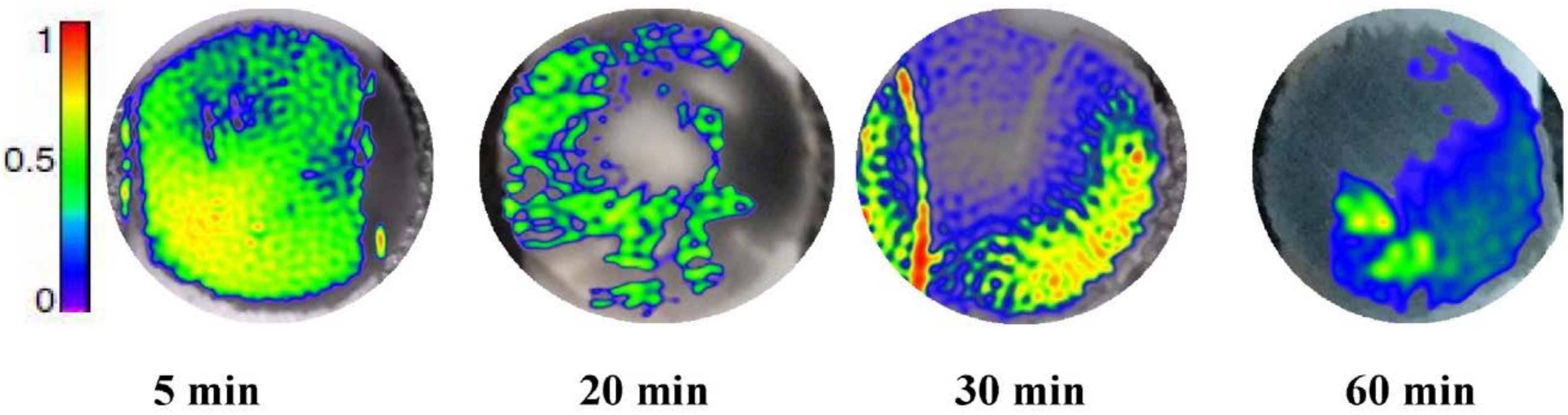
Time	min	0	5	10	20	30	60
Coke	wt%	6.5	6.4	6.2	5.7	5.2	4.3
Grey-scale digital image							



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Materials for Batteries

CHARACTERIZATION, IN OPERANDO

ACS Energy LETTERS

http://pubs.acs.org/journal/aelccp

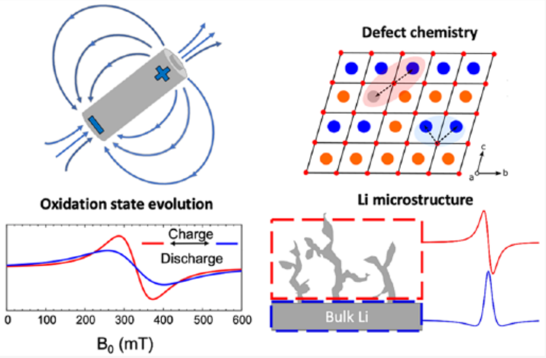
Rechargeable Batteries from the Perspective of the Electron Spin

Howie Nguyen and Raphaële J. Clément*

Cite This: *ACS Energy Lett.* 2020, 5, 3848–3859

Read Online

ABSTRACT: Rechargeable batteries generate current through the transfer of electrons between paramagnetic and/or metallic electrode materials. Electron spin probes, such as electron paramagnetic resonance (EPR) and magnetometry, can therefore provide detailed insight into the underlying energy storage mechanisms. These techniques have been applied *ex situ*, and more recently *operando*, to both intercalation- and conversion-type batteries. After briefly presenting the principles of EPR and magnetometry, this Focus Review provides a critical discussion of recent studies that leverage these tools to understand the local structure, defect chemistry, and charge−discharge and failure mechanisms of rechargeable batteries. Challenges in data collection and interpretation are addressed, and strategies to facilitate EPR spectral assignment and expand the scope of EPR and magnetometry studies of battery systems are suggested.



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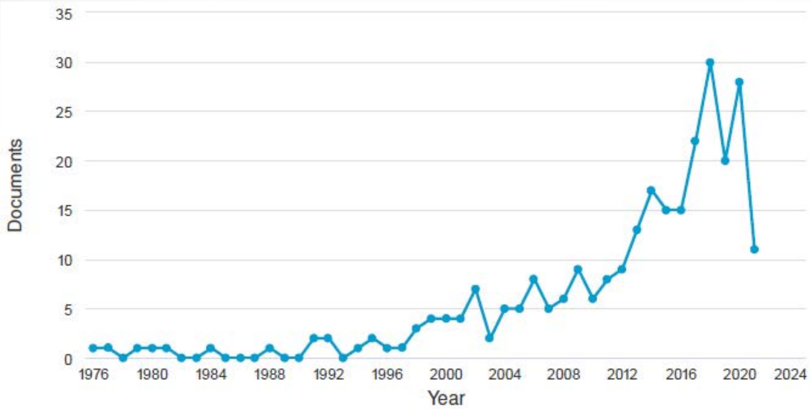
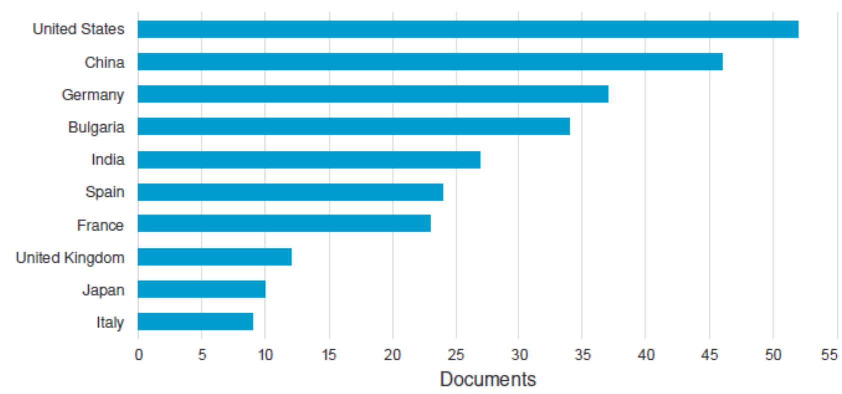
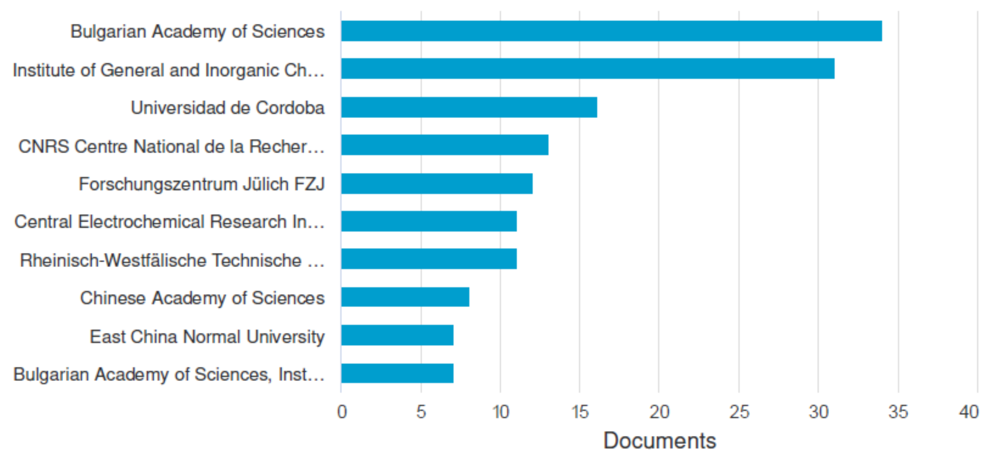
Benchmark

- <u>EPR Material for Battery</u>







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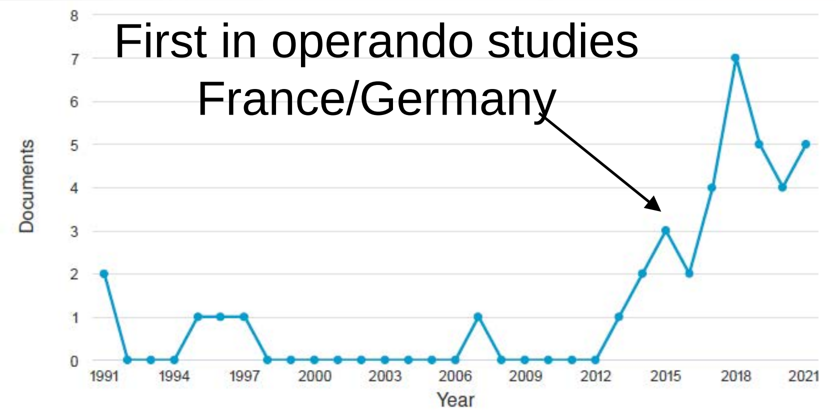
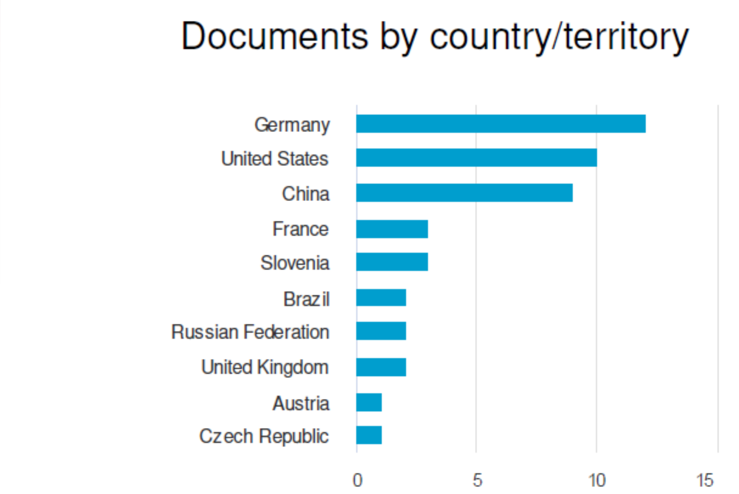
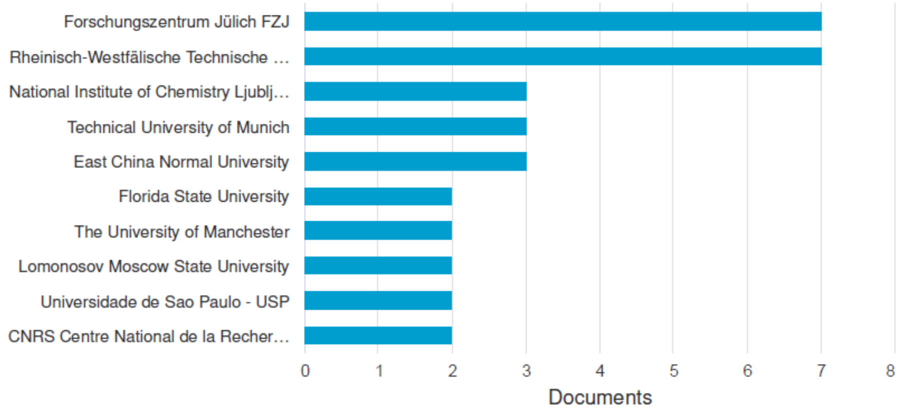
Benchmark

- **EPR Material for Battery in Operando**







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Design of the battery and resonator for Operando EPR

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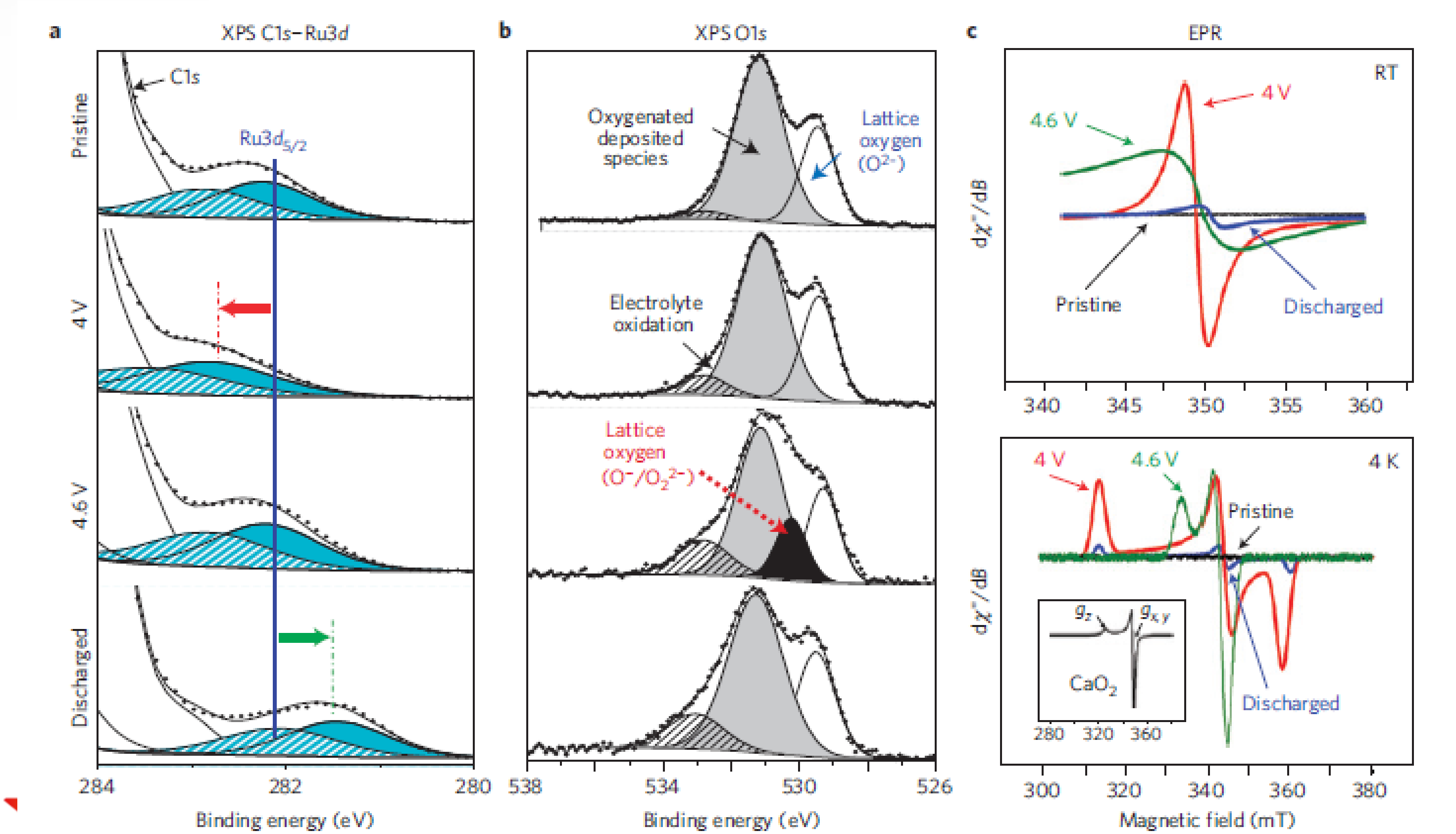
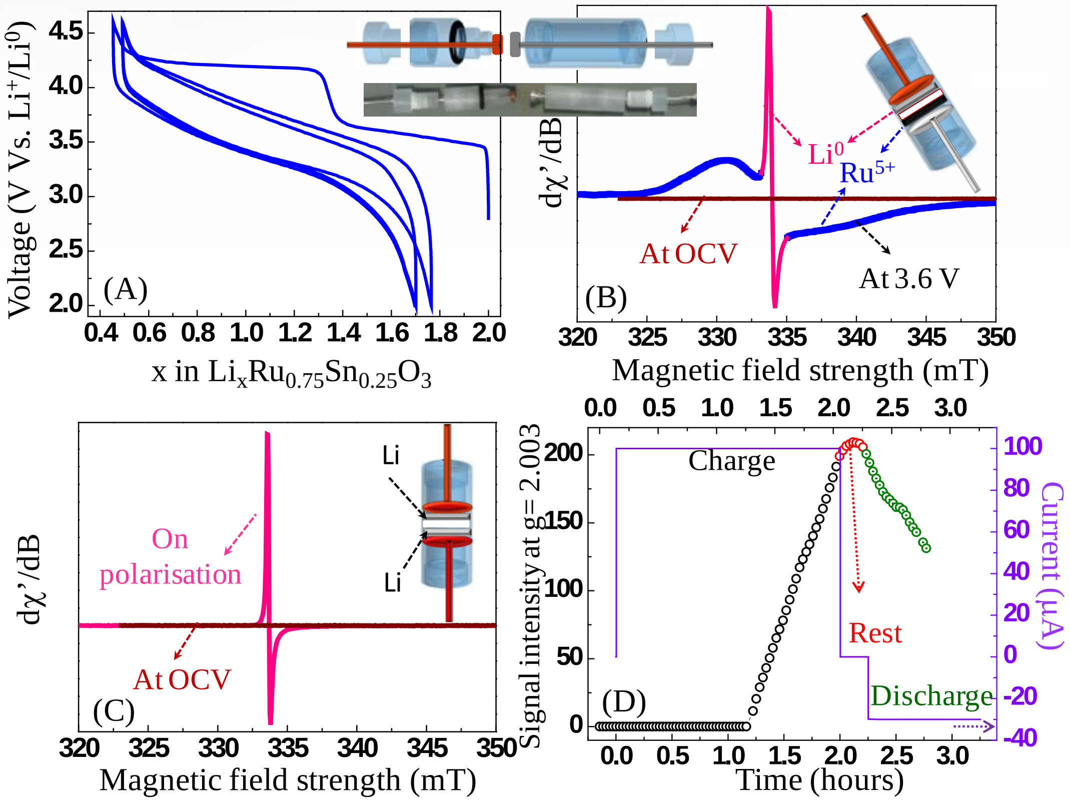
Ex-situ study

Material: $Li_2Ru_{0.5}Sn_{0.5}O_3$ ex-situ

Sathiya, M., G. Rousse, K. Ramesha, C. P. Laisa, H. Vezin, M. T. Sougrati, M-L. Doublet, et al. 2013. “Reversible Anionic Redox Chemistry in High-Capacity Layered-Oxide Electrodes.” *Nature Materials* 12 (9), 827–35.



Pushing the limits : operando EPR imaging



Sathiya, M., Leriche, J.-B., Salager, E., Gourier, D., Tarascon, J.-M., & Vezin, H. (2015). Electron paramagnetic resonance imaging for real-time monitoring of Li-ion batteries. *Nature Communications*, *6*, 6276.

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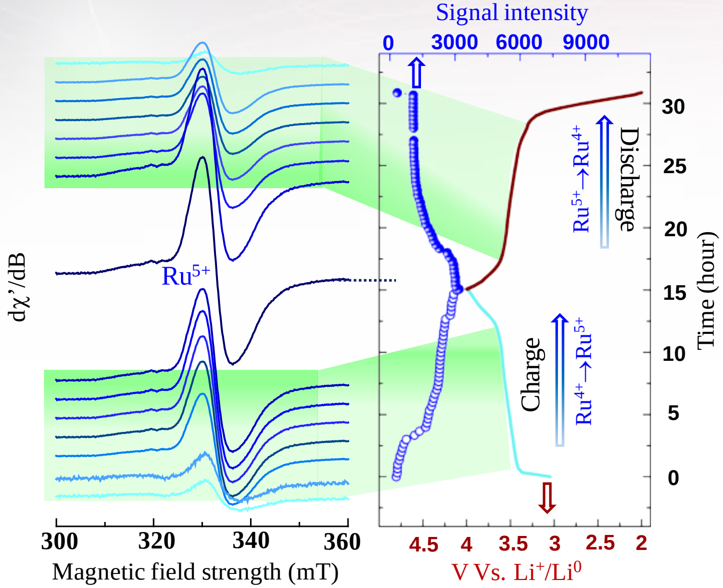
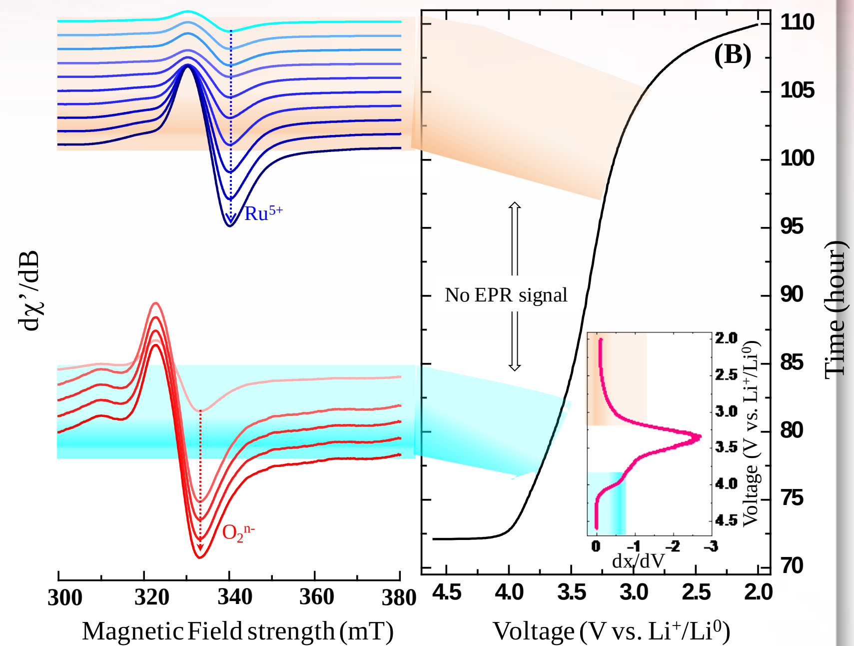
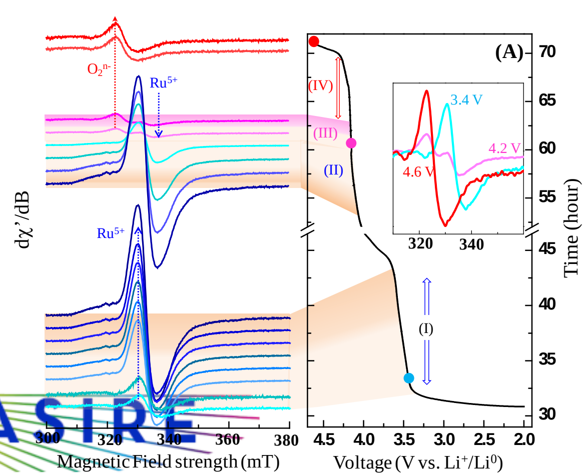
Redox/chemical state during battery driving



charge

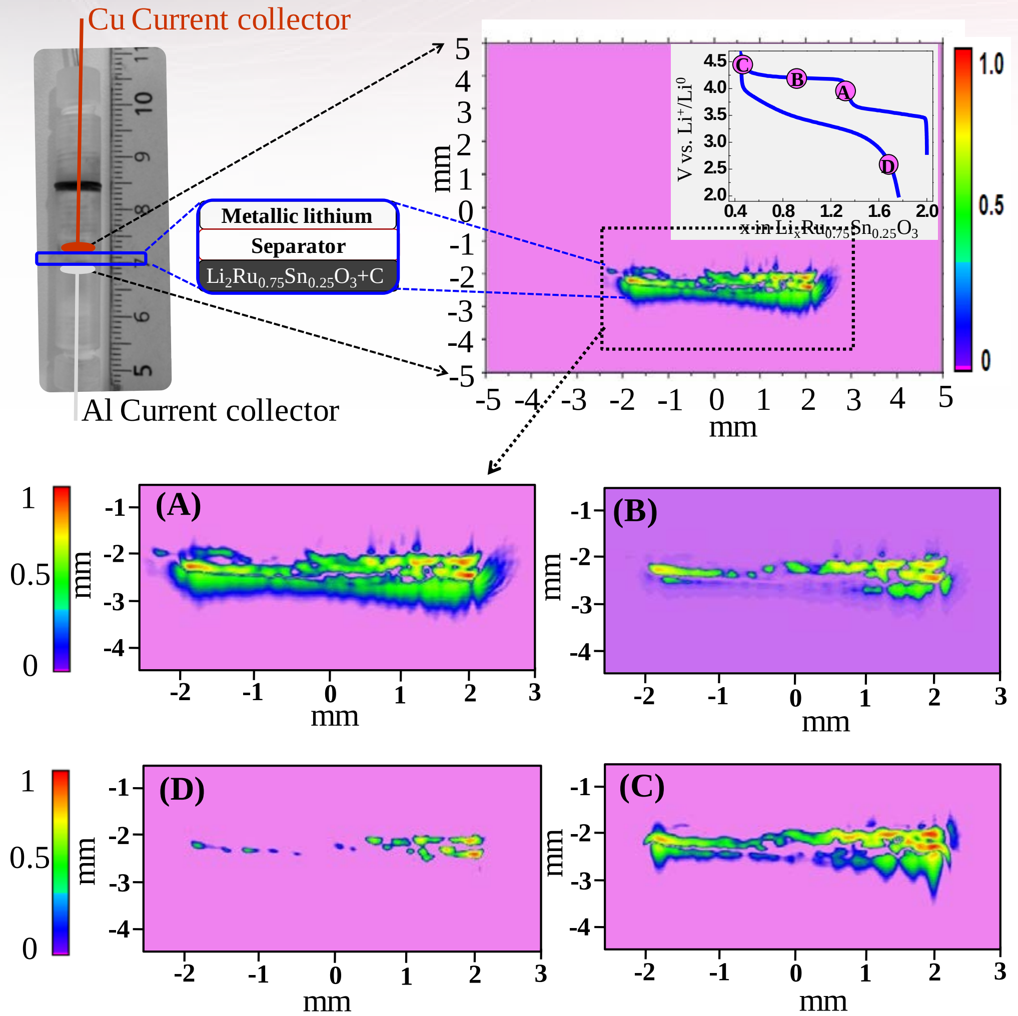


discharge



Sathiya, M., Leriche, J.-B., Salager, E., Gourier, D., Tarascon, J.-M., & Vezin, H. (2015). Electron paramagnetic resonance imaging for real-time monitoring of Li-ion batteries. *Nature Communications*, *6*, 6276.

Spatial distribution of species



Sathiya, M., Leriche, J.-B., Salager, E., Gourier, D., Tarascon, J.-M., & Vezin, H. (2015). Electron paramagnetic resonance imaging for real-time monitoring of Li-ion batteries. *Nature Communications*, *6*, 6276.

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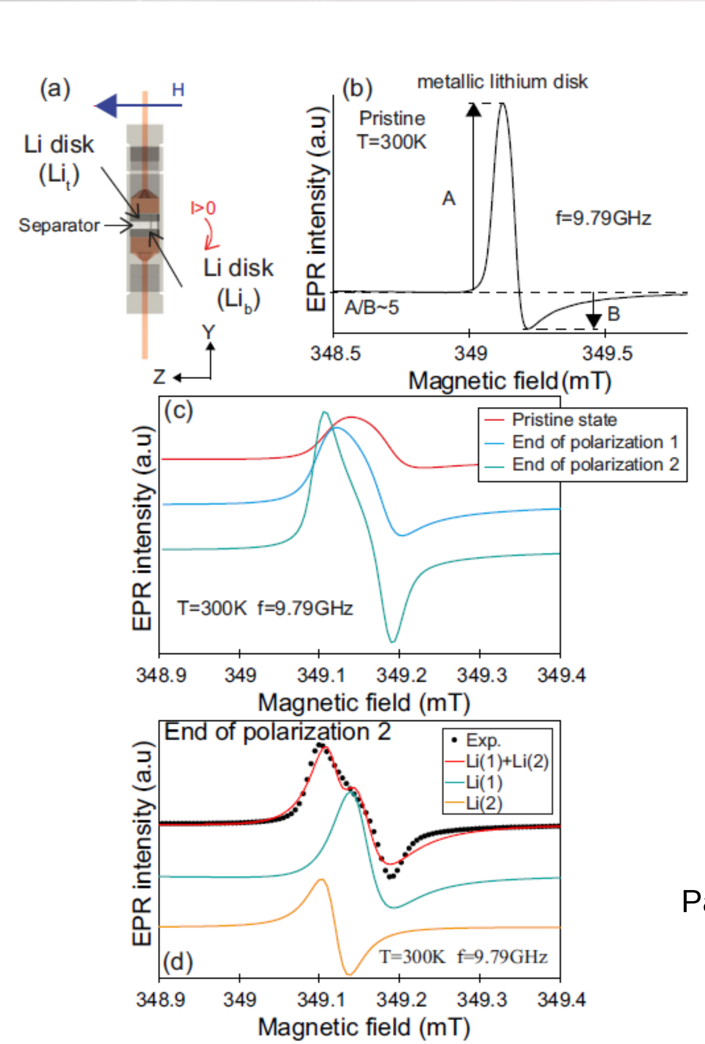
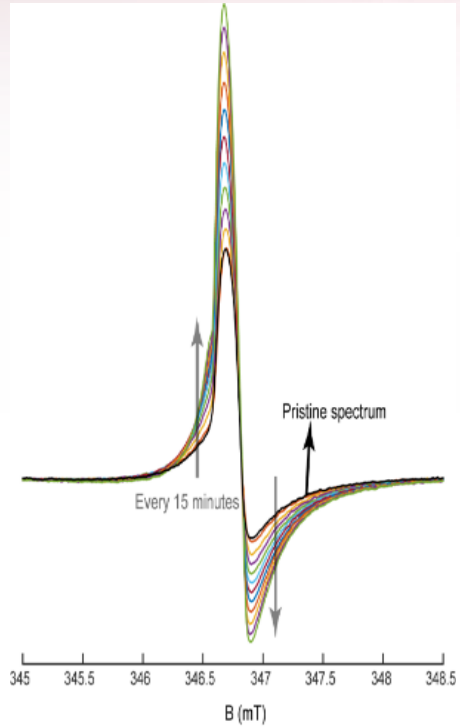
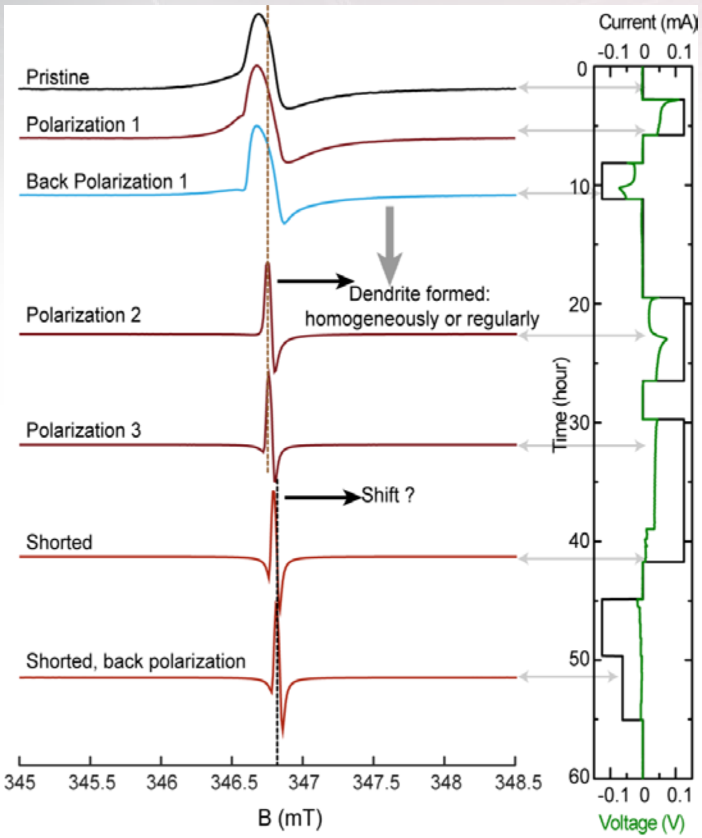
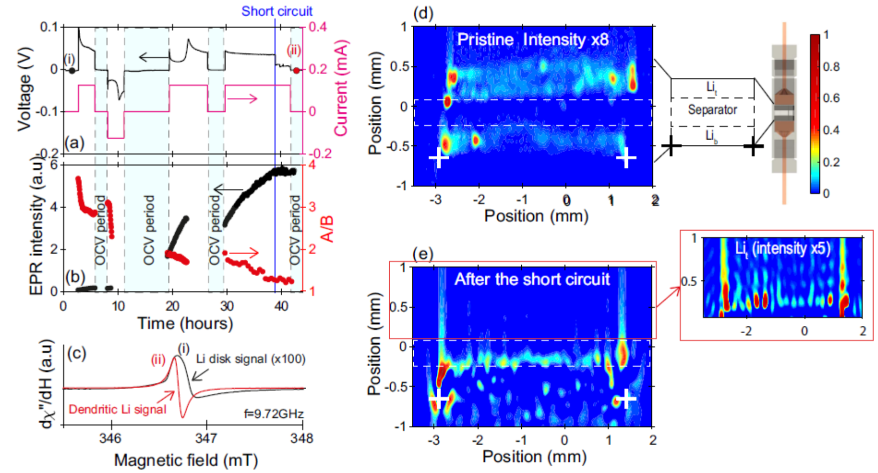
In situ (Operando) EPR follow the formation and distribution of the Lithium dendrite





Dutoit, Charles-Emmanuel, Mingxue Tang, Didier Gourier, Jean-Marie Tarascon, Hervé Vezin, and Elodie Salager, 'Monitoring Metallic Sub-Micrometric Lithium Structures in Li-Ion Batteries by in Situ Electron Paramagnetic Resonance Correlated Spectroscopy and Imaging', *Nature Communications*, 12.1 (2021), 1410





CW-EPR spectra of the Li//Li symmetric battery at different polarization stages, together with the electrochemical profile

Imaging of dendrites formation

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Change of spectral shape: change of Li particles sizes

Conclusions : new developments

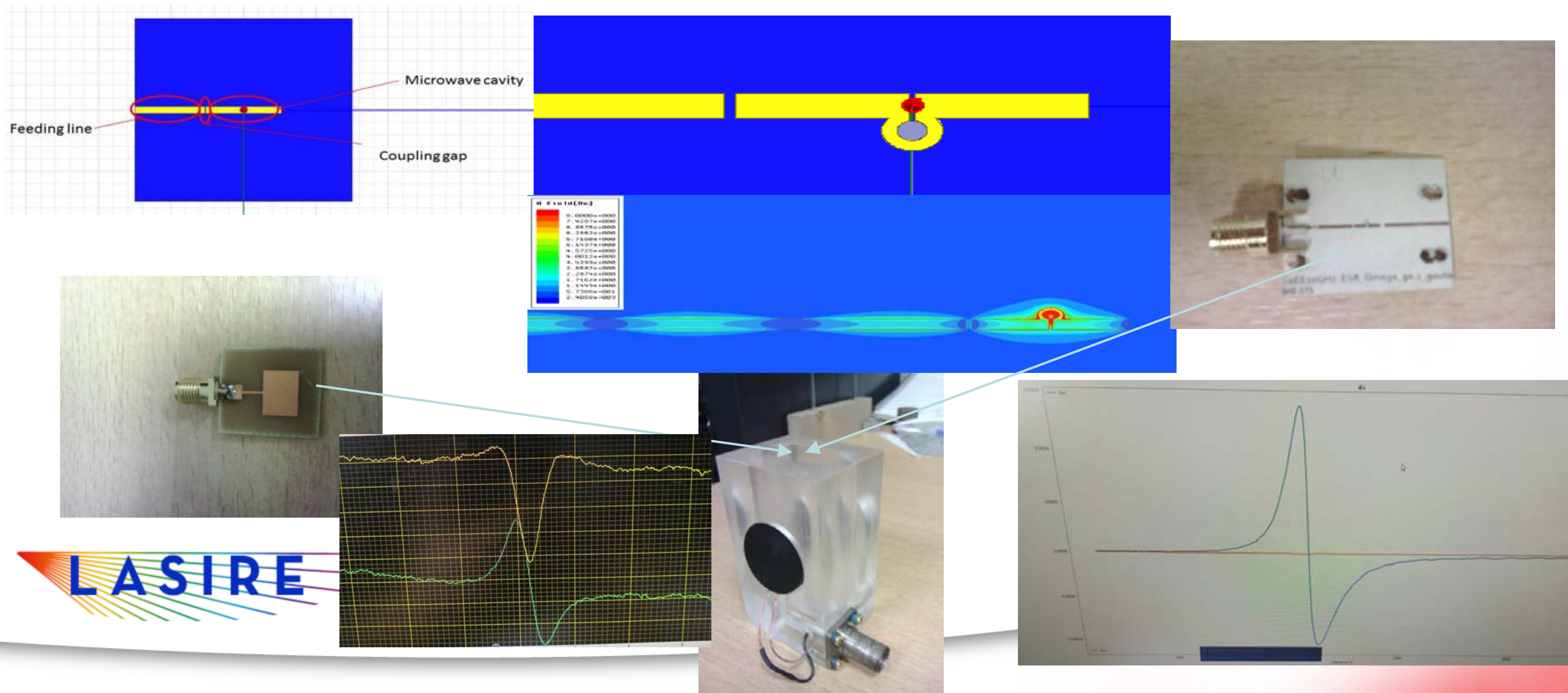
EPR is very sensitive spectroscopy (10^{12} spins/g)

New tools with EPR imaging

Bulk spectroscopy

PGSE imaging combined with micro/nanostrip resonators

The futur : resolution at nm scale and drastic increase of sensitivity (10^8 spins/g)



Merci pour votre attention