

Nondestructive Diagnostics of Battery Cells by MRI

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NEW YORK UNIVERSITY



*predict failures,
lifetimes
early
non-destructively
quickly*

Can we detect dendrites,
soft shorts, electrolyte
distribution, uneven
SOC, metal particles ...?

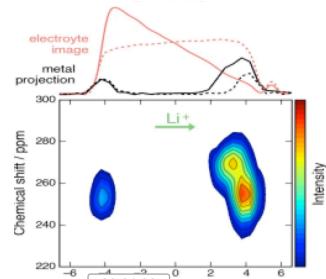
MRI



In-situ (operando) NMR/MRI

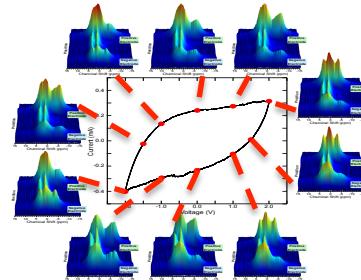
Li-dendrite visualization

- ${}^7\text{Li}$ MRI / CSI
- ${}^1\text{H}$ MRI



Supercapacitors

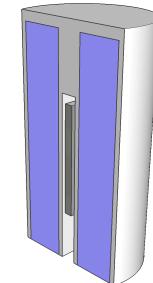
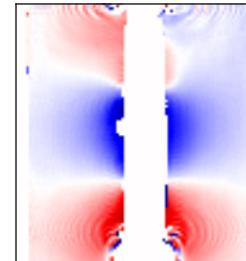
- ${}^1\text{H}$ / ${}^{11}\text{B}$ MRI



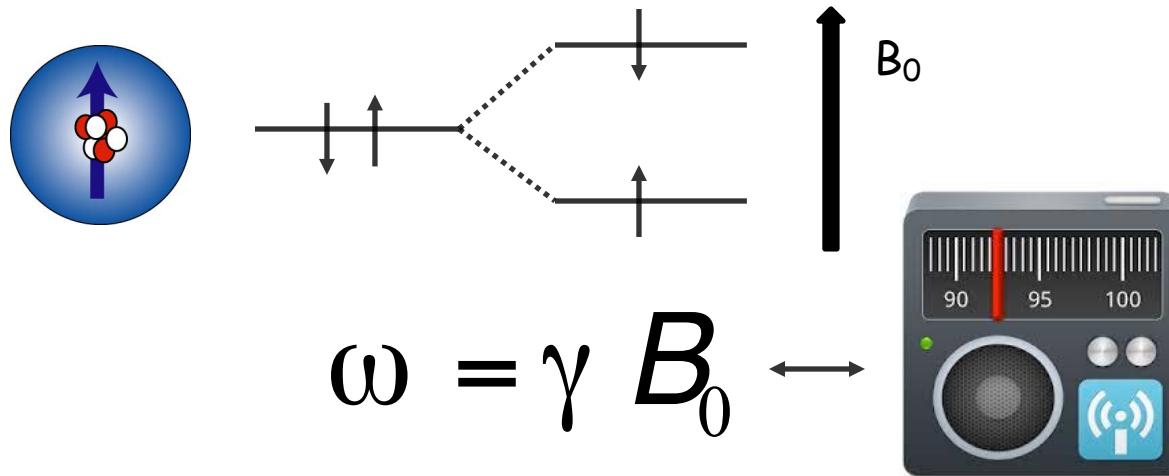
“In real life”

Commercial-type cell analysis

- SOC
- SOH
- Current distribution



NMR

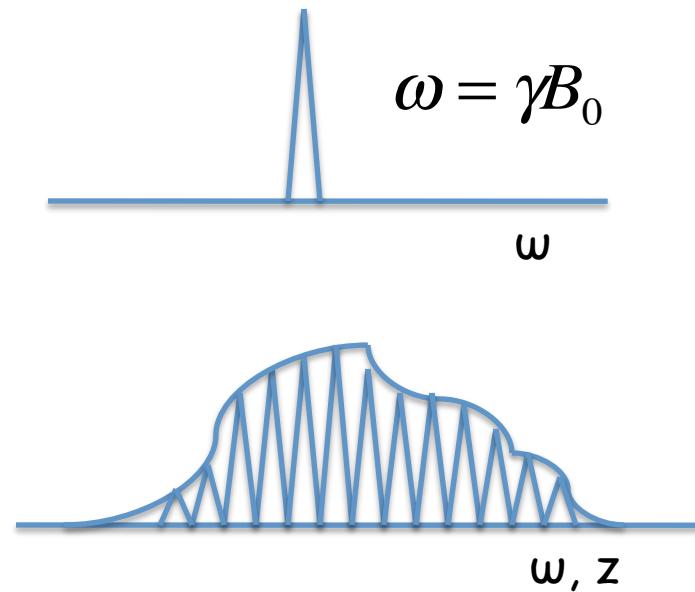
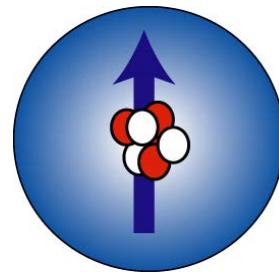


Chemical shift: varying electron density
→ small changes in frequency

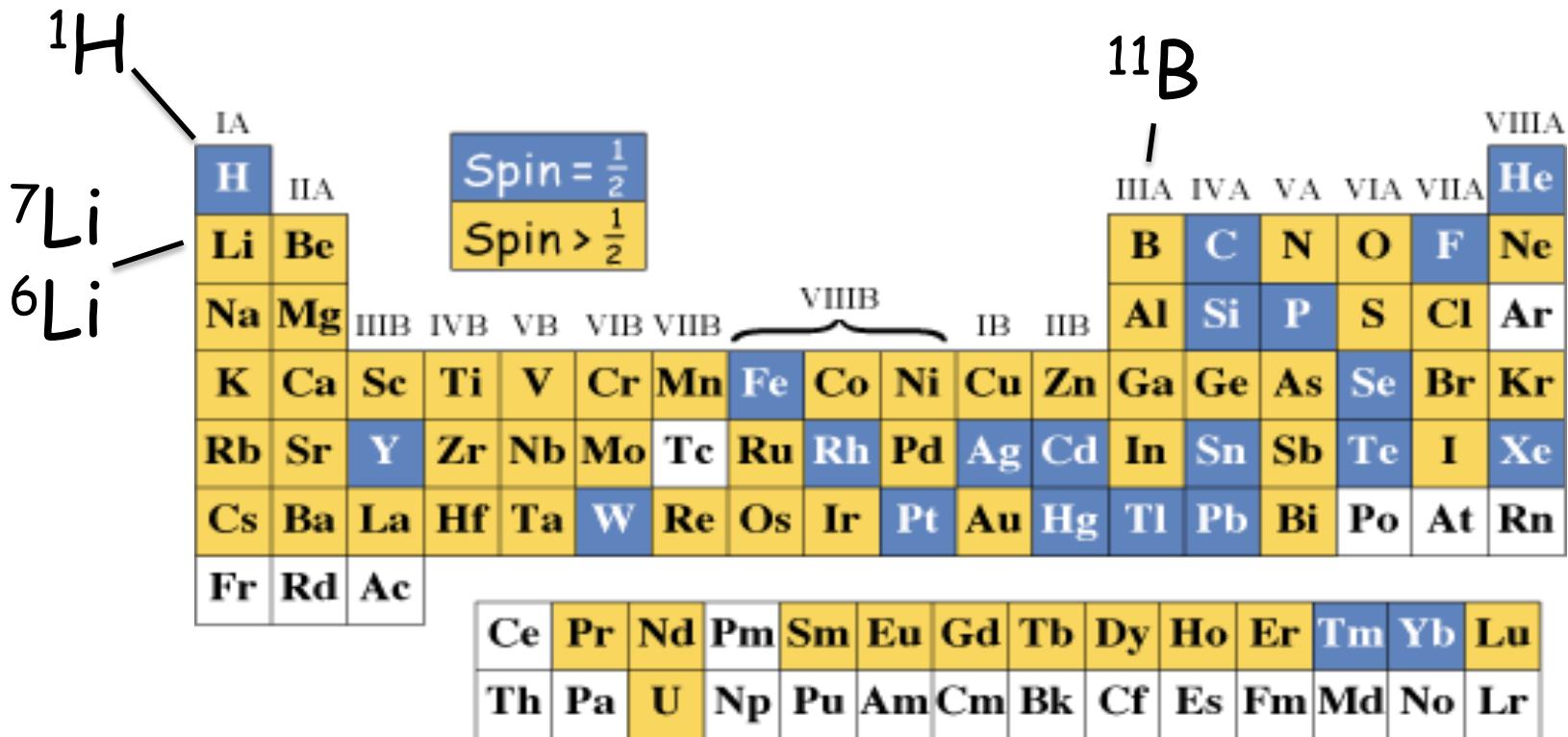
NMR and MRI

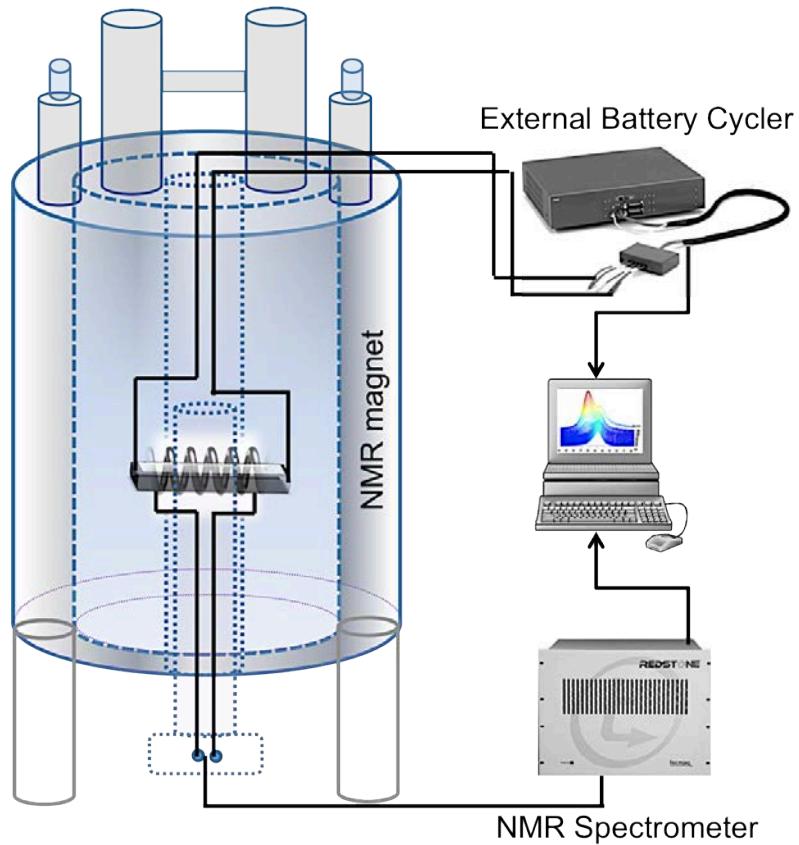
$$B_0 + G^* z$$

The diagram illustrates the total magnetic field B_0 as the sum of two components: the static magnetic field G^* and the gradient field z . A large vertical blue arrow labeled B_0 is shown at the top. Below it, a plus sign (+) is followed by a vertical stack of arrows. From top to bottom, there is an upward arrow, a small diamond-shaped arrow pointing up and to the right, a downward arrow, and a large downward arrow. This visualizes how the total field is the vector sum of the static field and the gradient field.



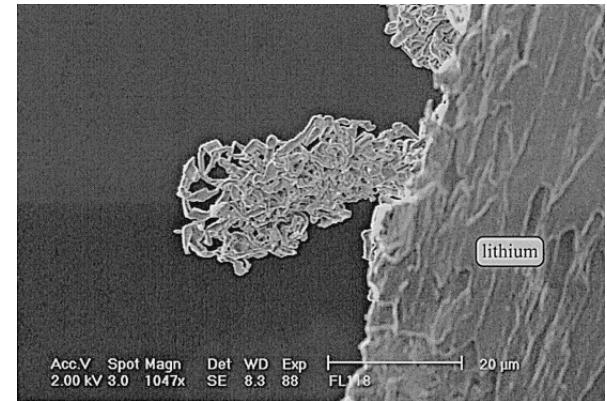
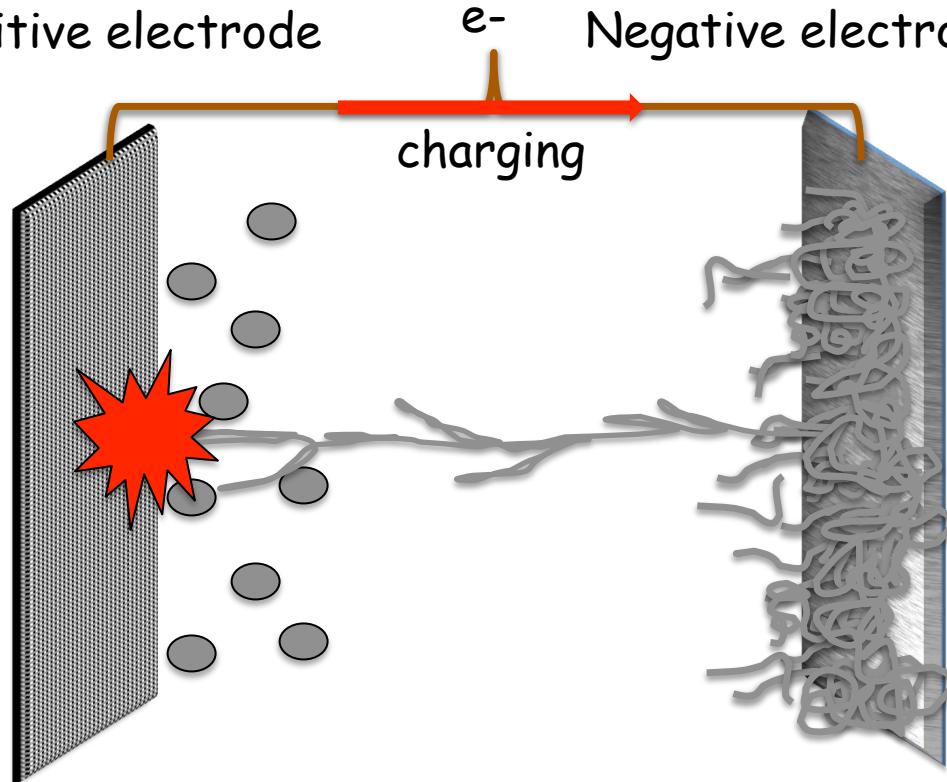
NMR accessible nuclei





Li plating / Li dendrites

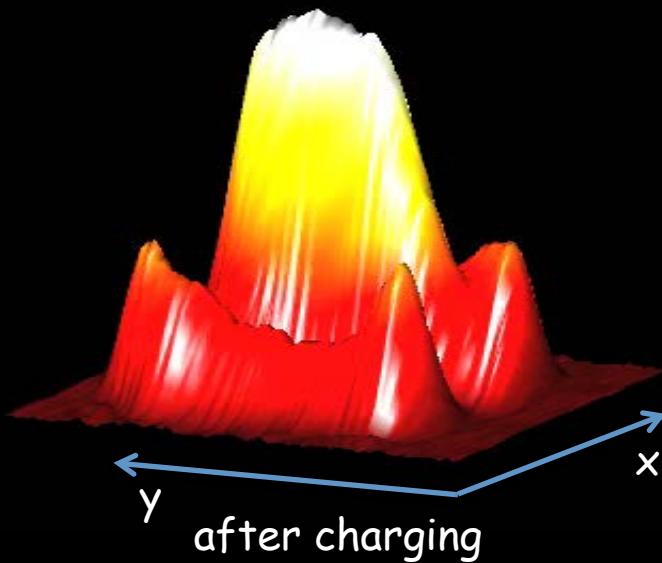
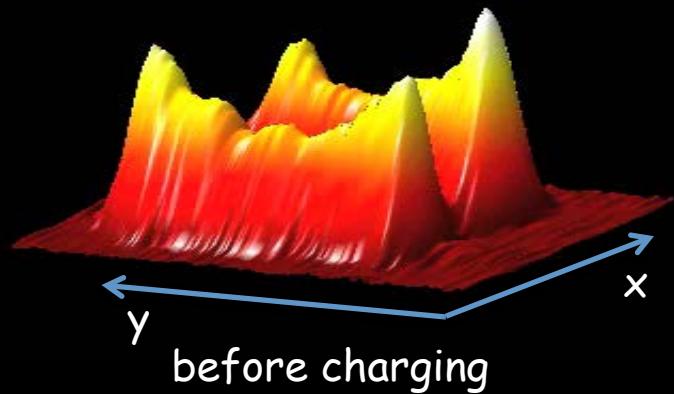
Positive electrode e- Negative electrode (Lithium)



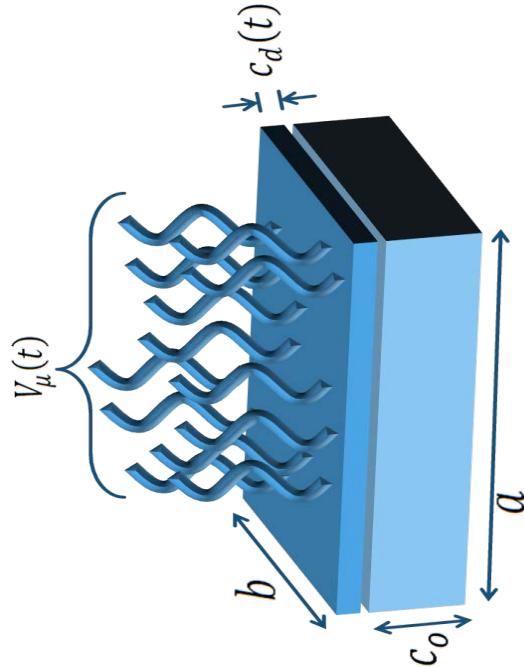
Orsini et al,
J Pow Src 76, 1998, 19

Hee Jung Chang

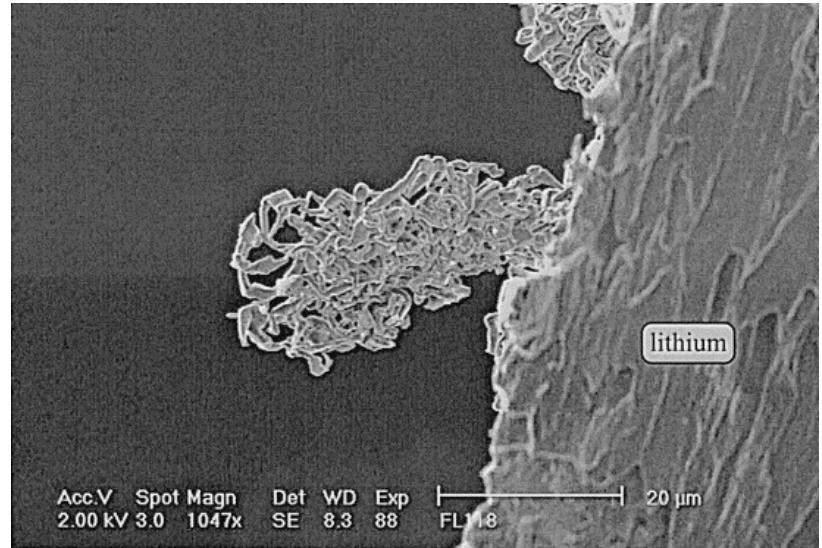
Lithium MRI of Batteries



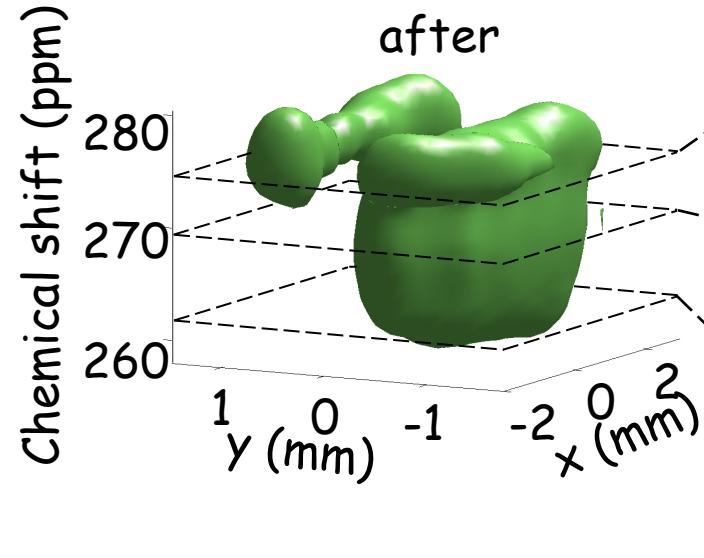
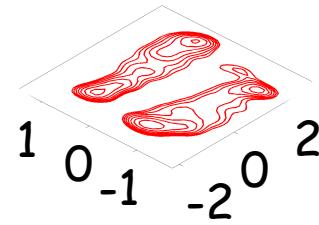
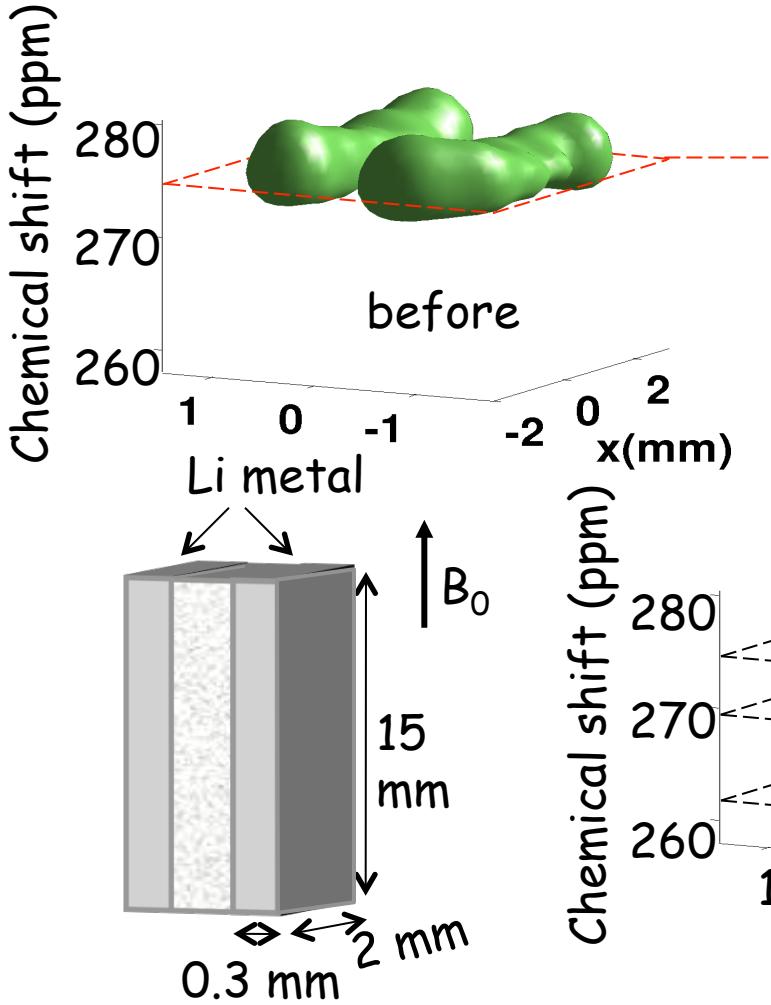
Li-dendrites on electrode



Bhattacharya et al,
Nat. Mat. 9, 2010, 504

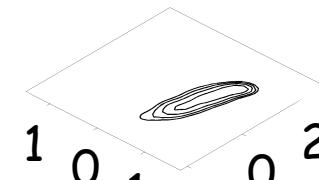
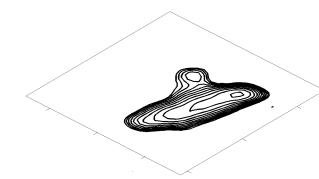
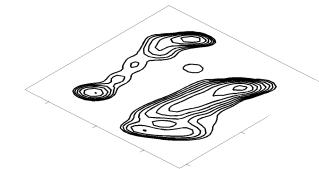


Orsini et al,
J Pow Src 76, 1998, 19

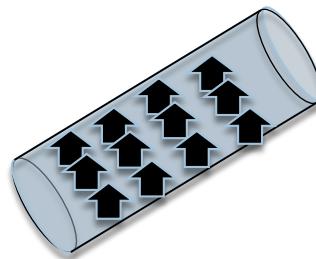
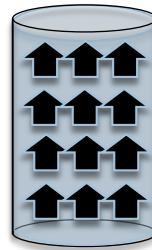


^{7}Li CSI of Li-ion batt.

Chandrashekhar et al.
Nat Mater, 11, 2012, 311



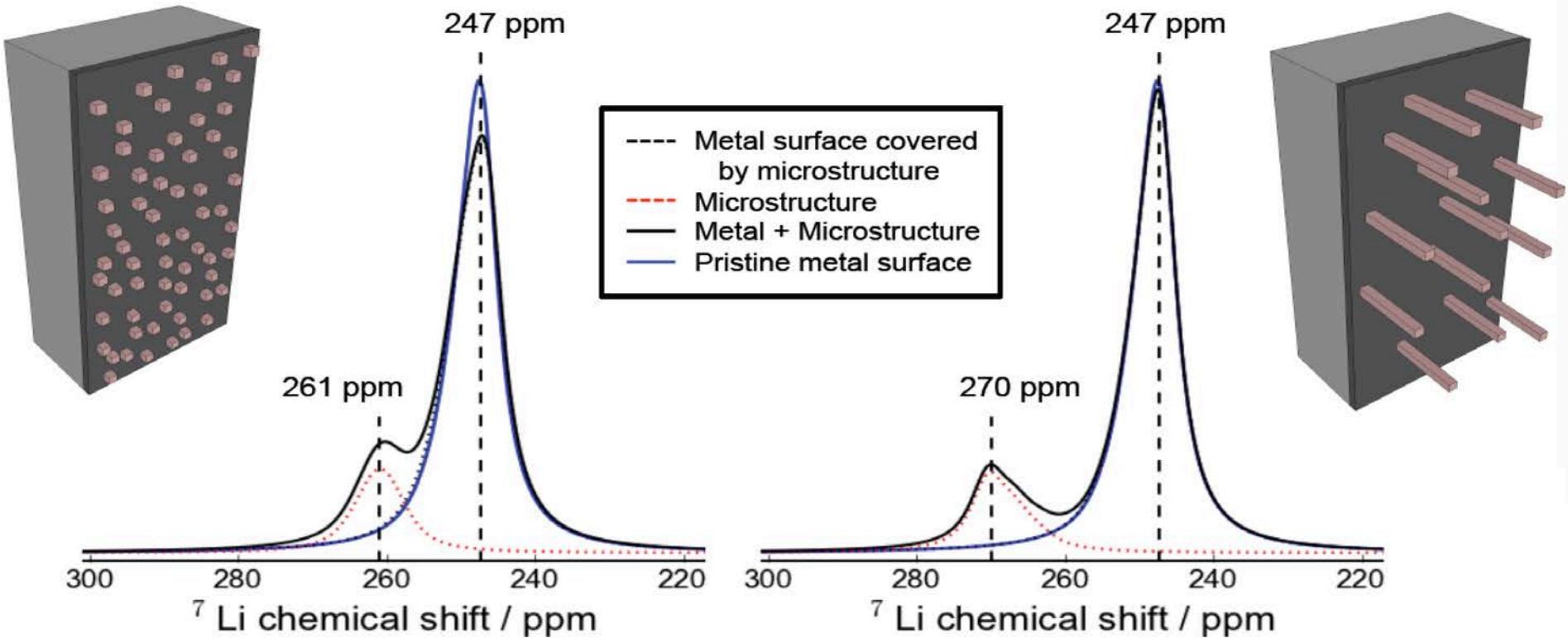
Superresolution Information: Chemical and Susceptibility shifts



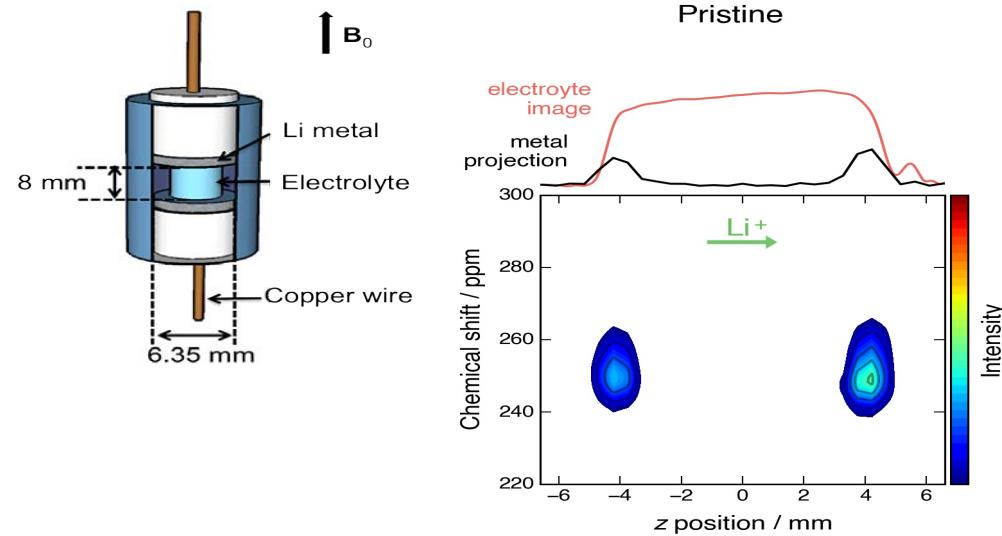
χ

(a) Mossy microstructure

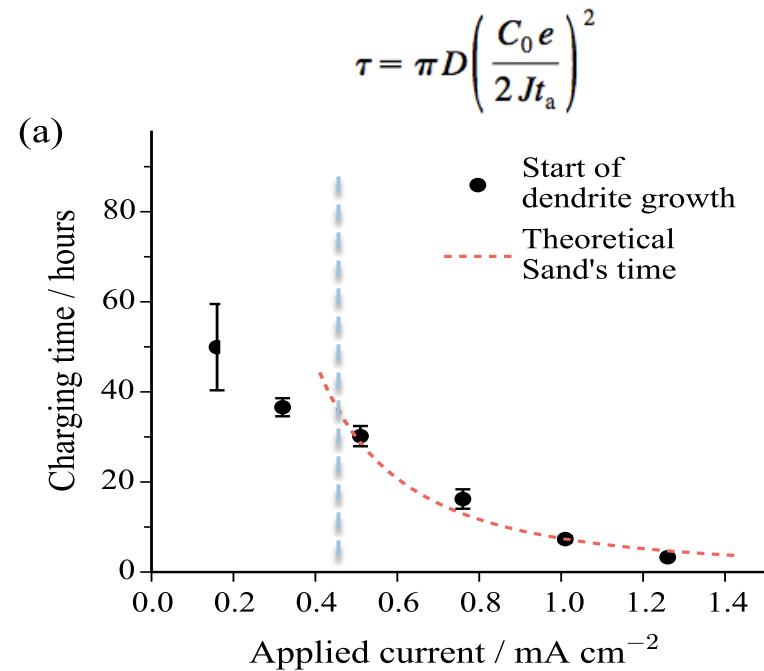
(b) Dendritic microstructure



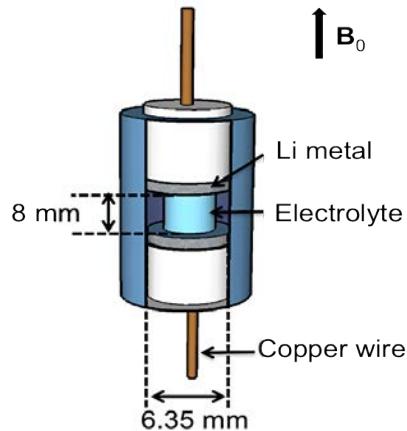
Studying dendrite growth models



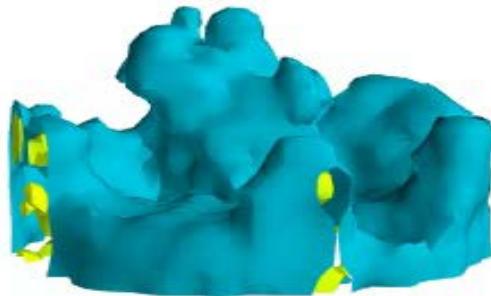
H.J. Chang et al, JACS 2015, 137, 15209



Indirect MRI of dendrite growth



^1H 3D FLASH
'negative'
image



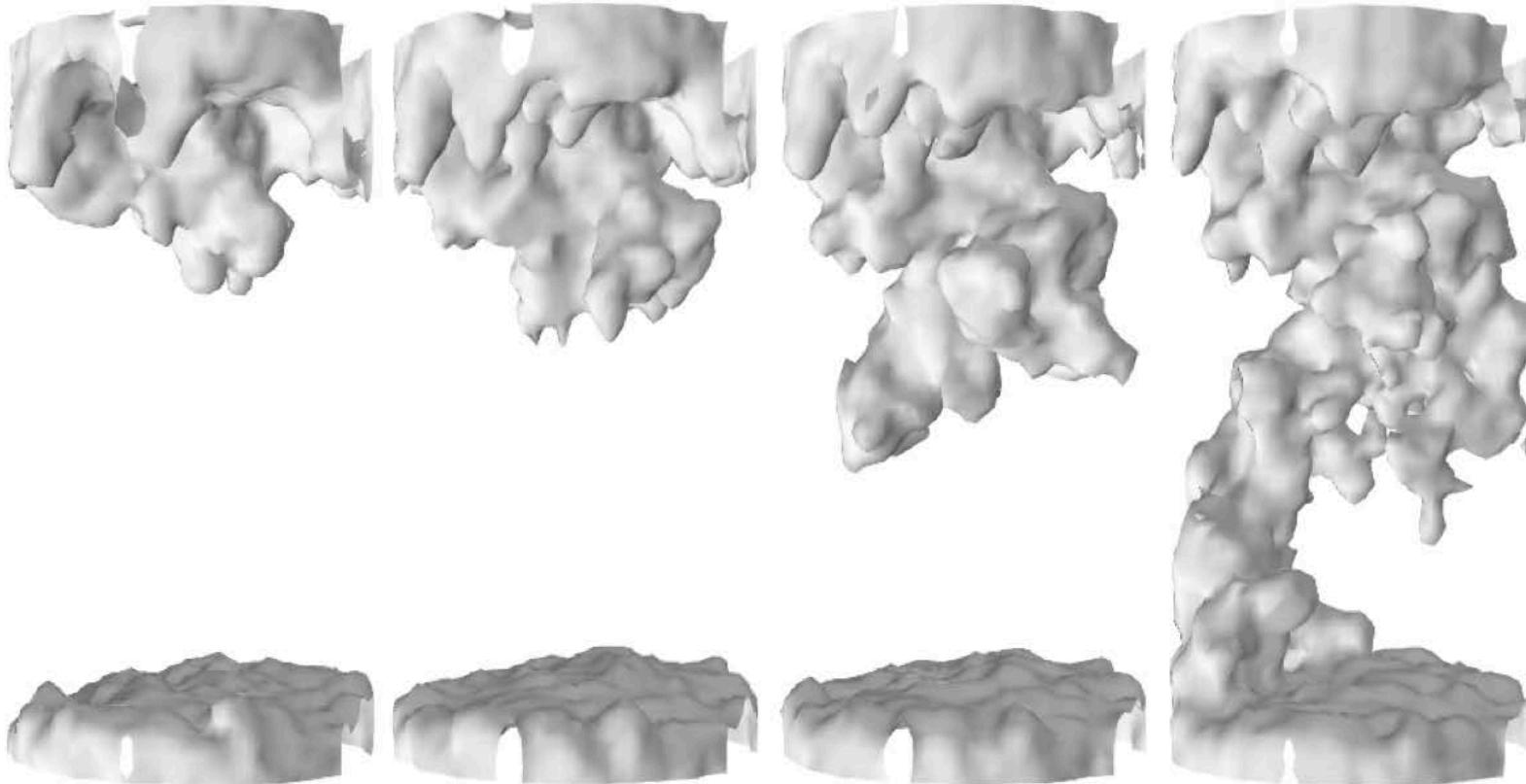
Ilott et al.,
PNAS, 2016,
113, 10779-84

Start

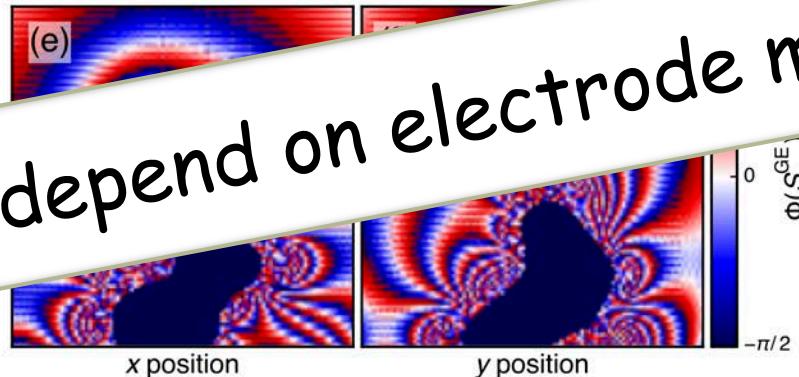
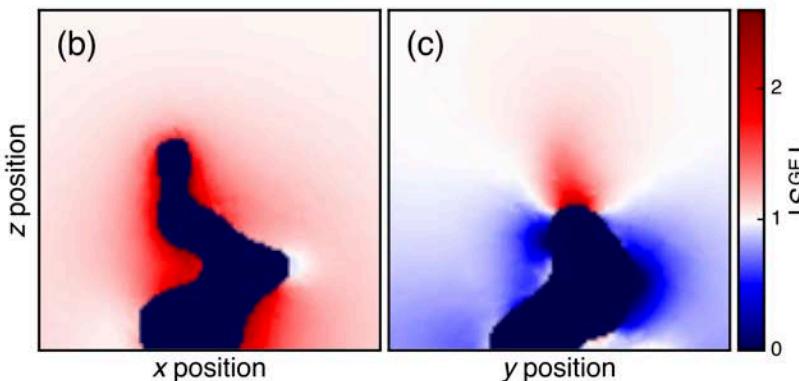
7.5 hours

15.8 hours

26.1 hours



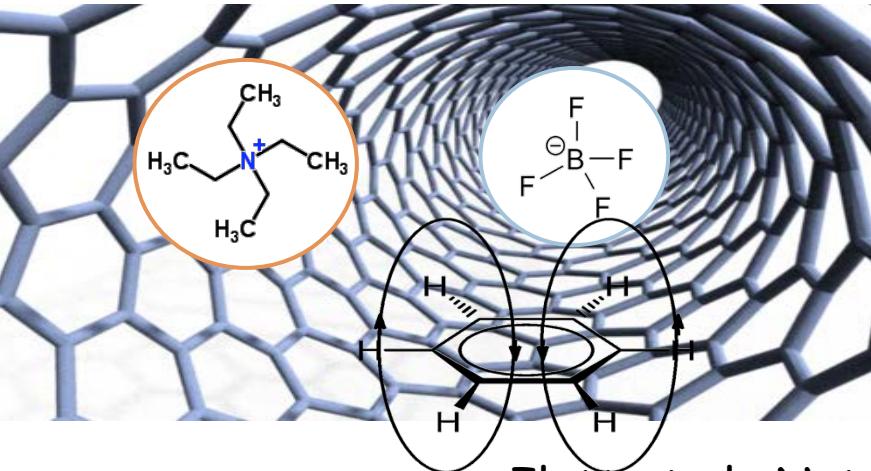
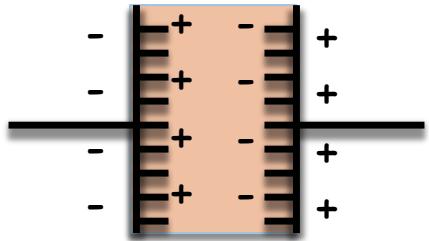
~20-fold amplification from field distortions!



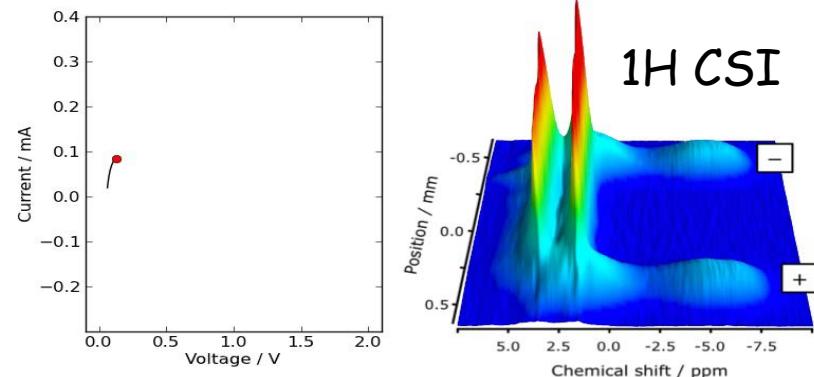
Does not depend on electrode material

Ilott et al.,
PNAS, 2016,
113, 10779-84

Supercapacitors



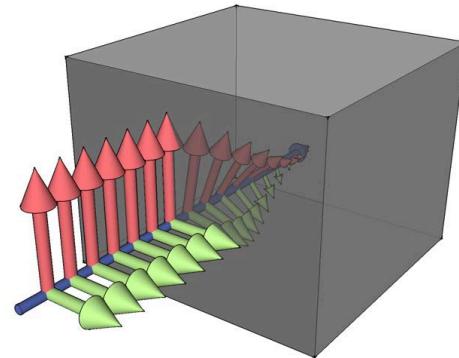
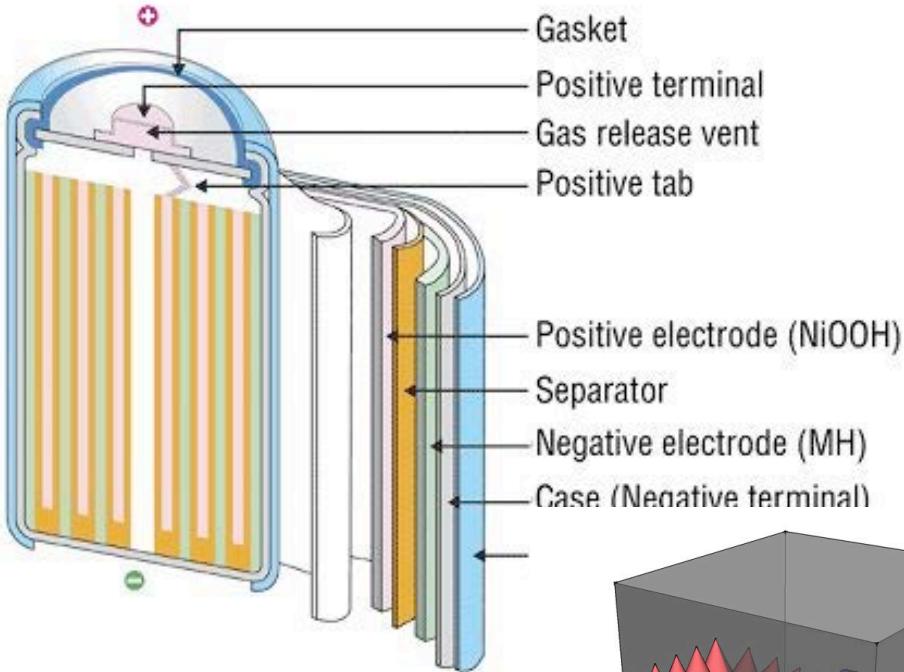
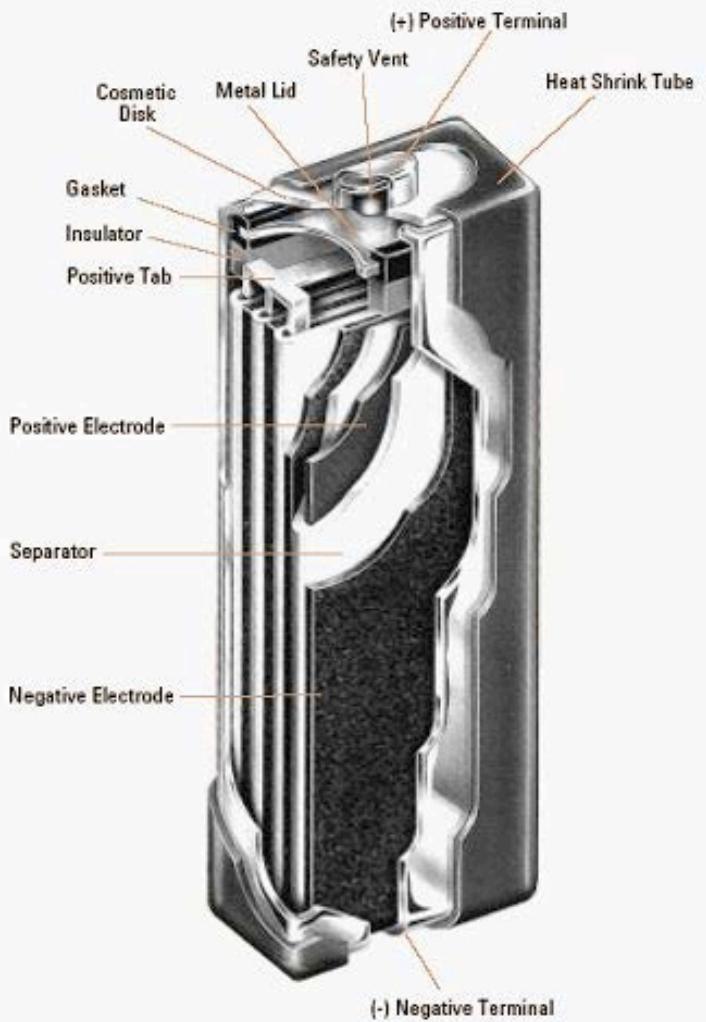
Ilot et al., Nat. Comm., 5, 2014, 4536



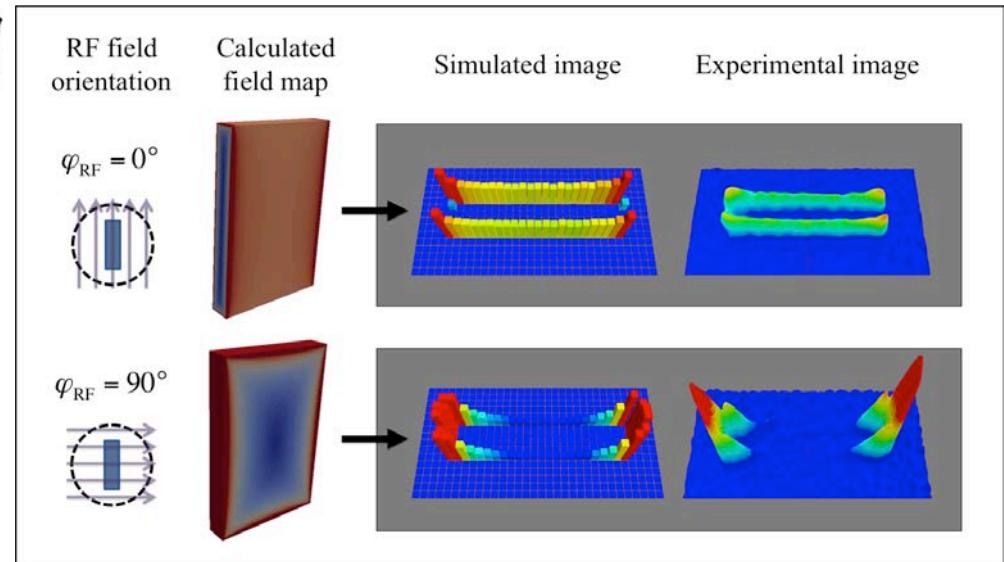
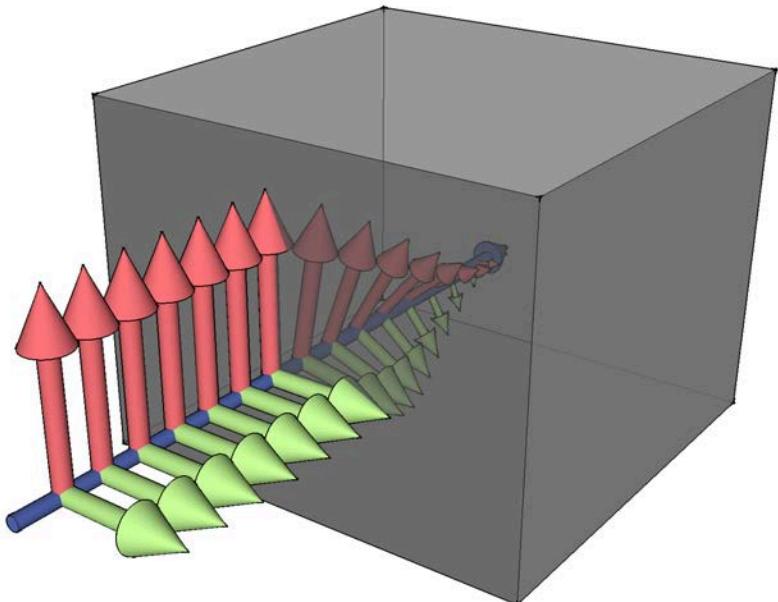


“In real life”





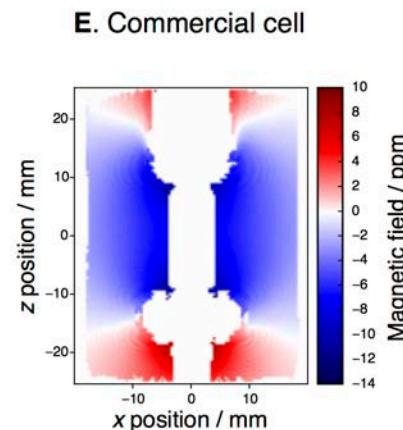
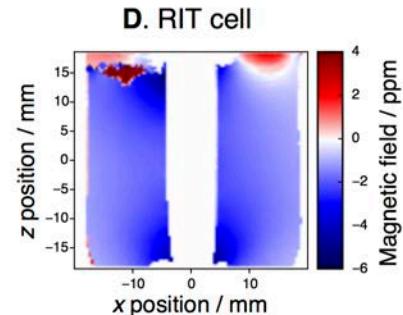
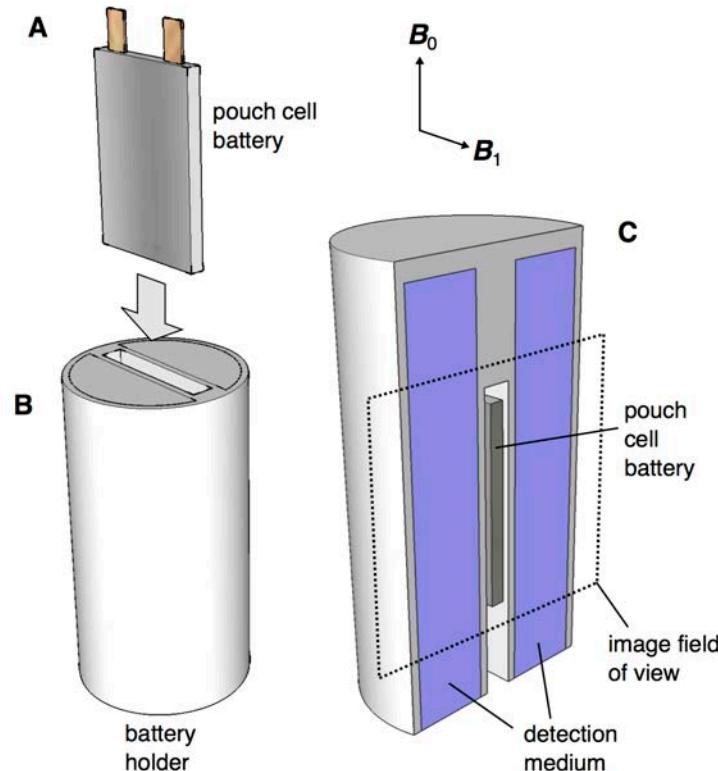
RF penetration into metal: skin effect



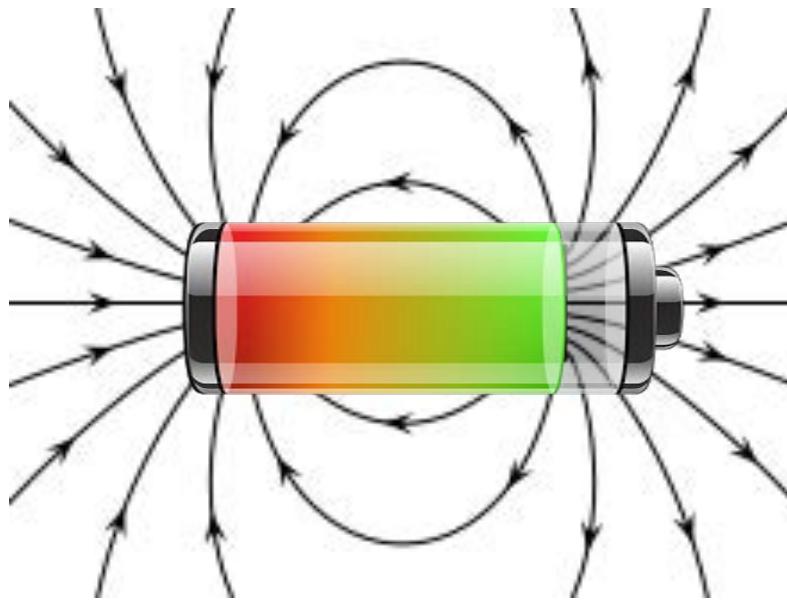
$$\delta = \frac{1}{\sqrt{\pi \mu_r \mu_0 \sigma f}} \text{ skin depth}$$

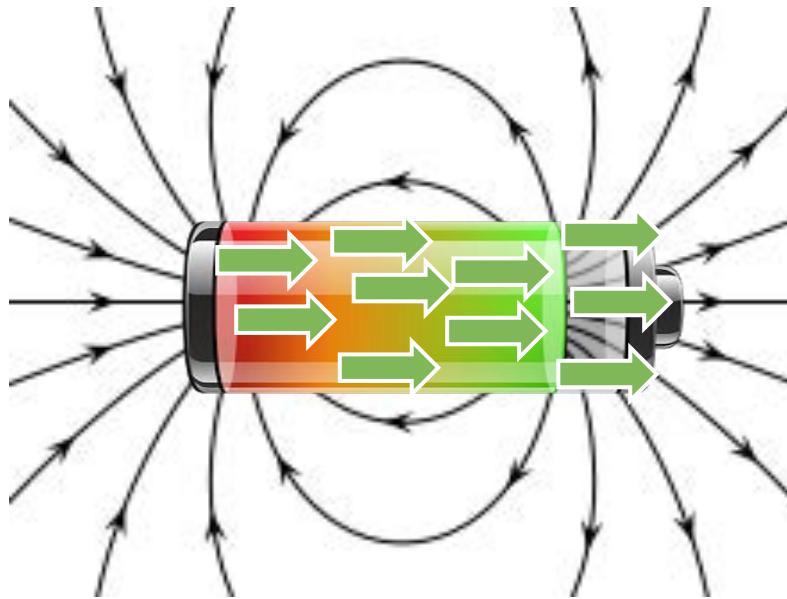
Ilott et al., JMR, 245, 2014, 143-149

Inside-out MRI



Ilott, et al, *Nat Comm* 9:1776, 2018

B_0
→

B_0


Magnetic Susceptibility

PHYSICAL REVIEW B 77, 075119 (2008)

Magnetism and structure of Li_xCoO_2 and comparison to Na_xCoO_2

J. T. Hertz,¹ Q. Huang,² T. McQueen,¹ T. Klimczuk,^{3,4} J. W. G. Bos,⁵ L. Viciu,¹ and R. J. Cava¹

Chem. Mater. **2007**, *19*, 4682–4693

Layered $\text{Li}_x\text{Ni}_y\text{Mn}_y\text{Co}_{1-2y}\text{O}_2$ Cathodes for Lithium Ion Batteries: Understanding Local Structure via Magnetic Properties

Natasha A. Chernova,^{*,†} Miaomiao Ma,[†] Jie Xiao,[†] M. Stanley Whittingham,[†]
Julien Breger,[‡] and Clare P. Grey[‡]

Magnetic Susceptibility effects

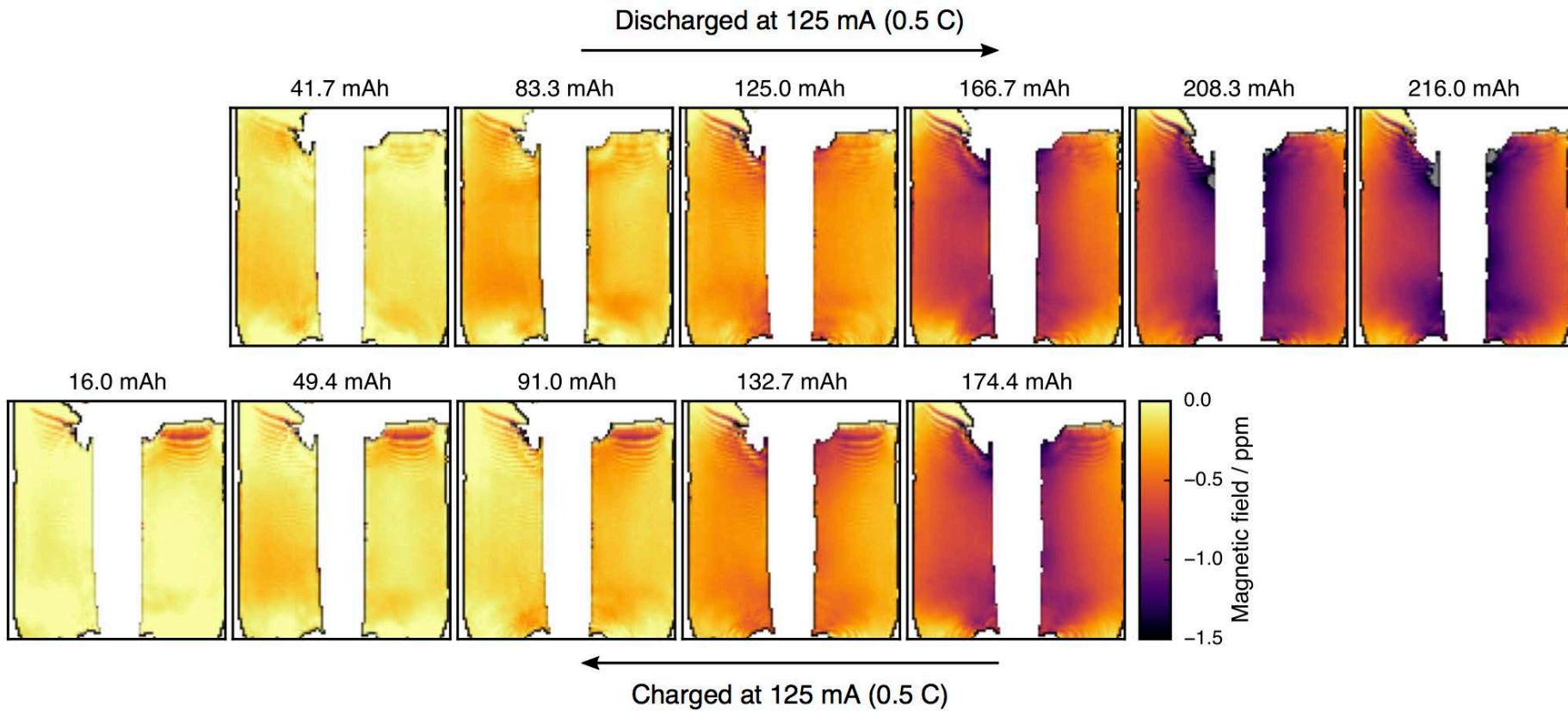




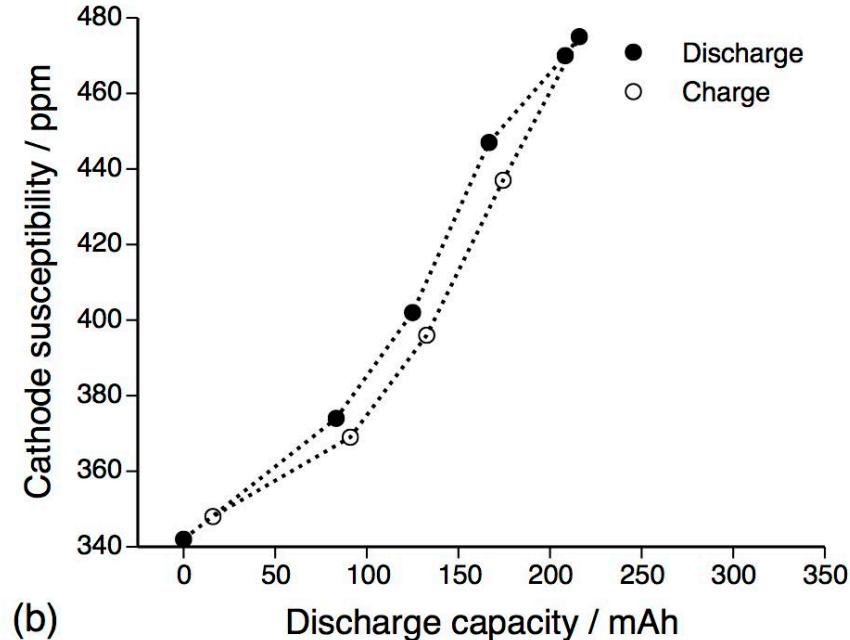
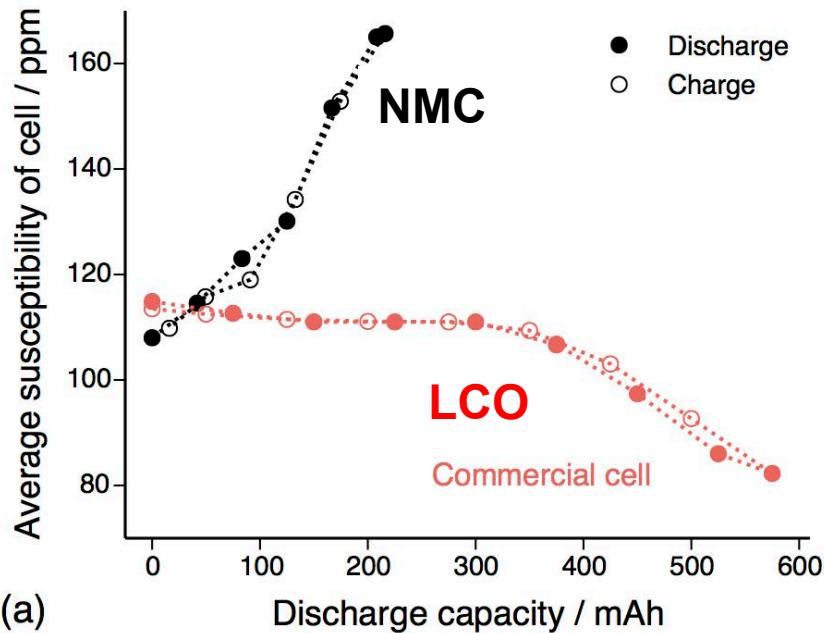




Magnetic field maps during discharge

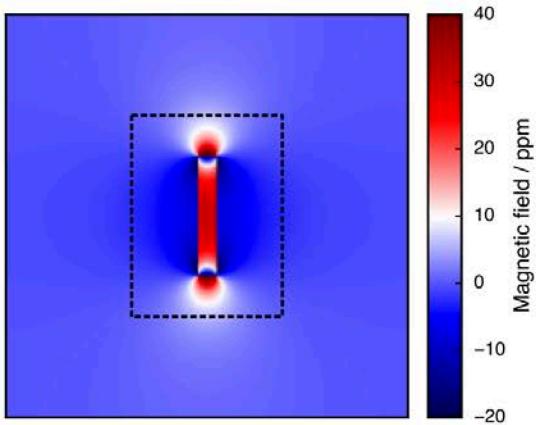


State of Charge from Susceptibility

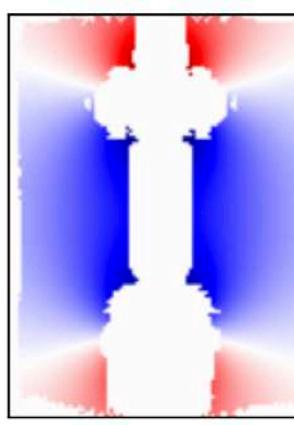


Susceptibility Inversion

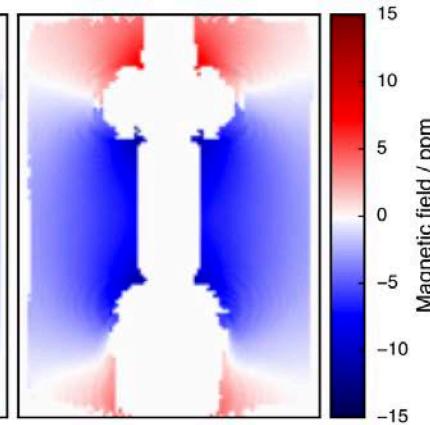
(a) Simulated Field Map,
 $B_{0,\text{sim}}(x,y)$



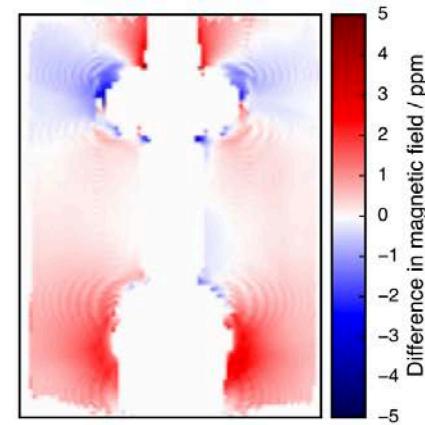
(b) Masked Simulated
Field Map, $B'_{0,\text{sim}}(x,y)$



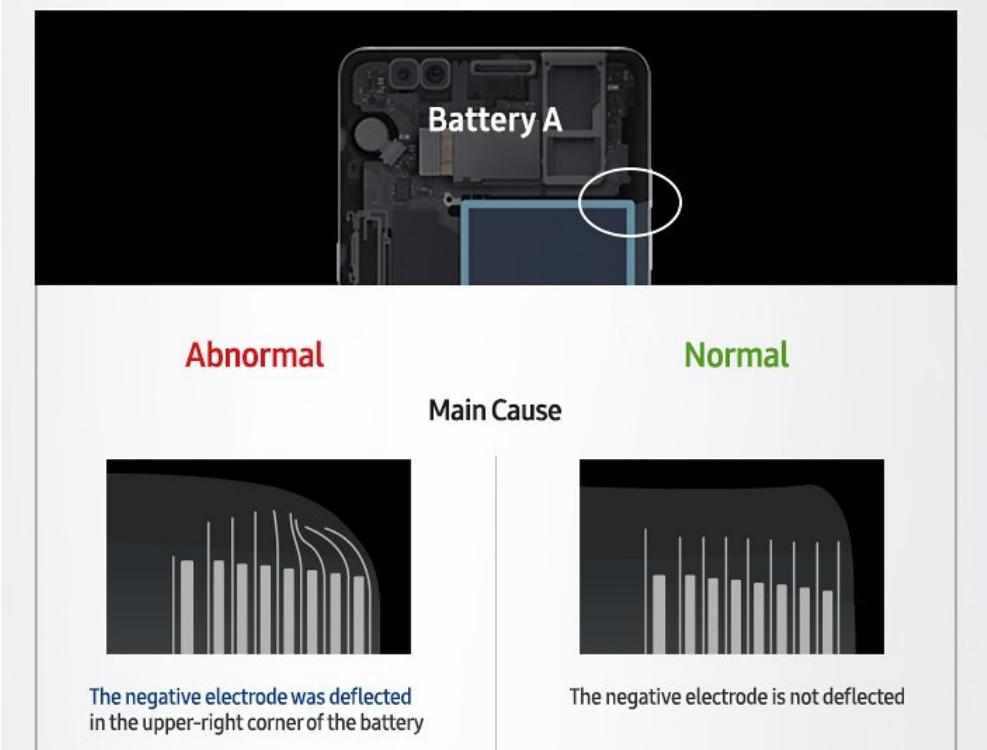
(c) Measured Field
Map, $B_{0,\text{exp}}(x,y)$



(d) Difference,
 $B'_{0,\text{sim}}(x,y) - B_{0,\text{exp}}(x,y)$



Samsung battery defects Jan 2017 press release





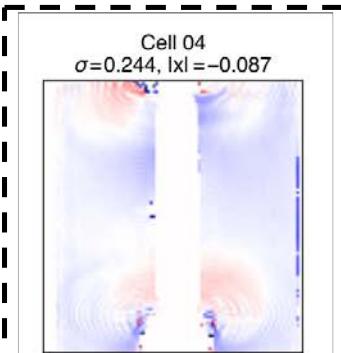
Battery
Prototyping
Center

Make cells
with defects

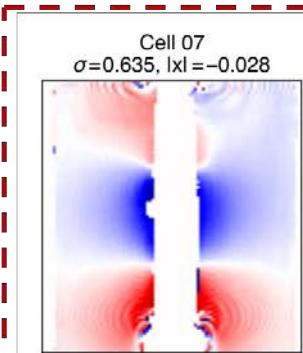


Defective cells

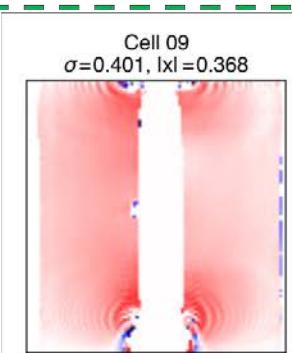
NON-DEFECT



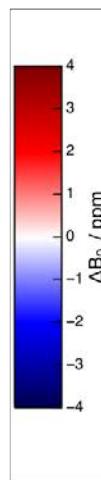
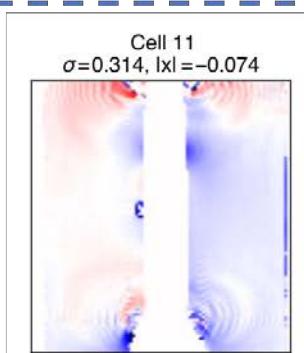
FOLDED
ELECTRODE

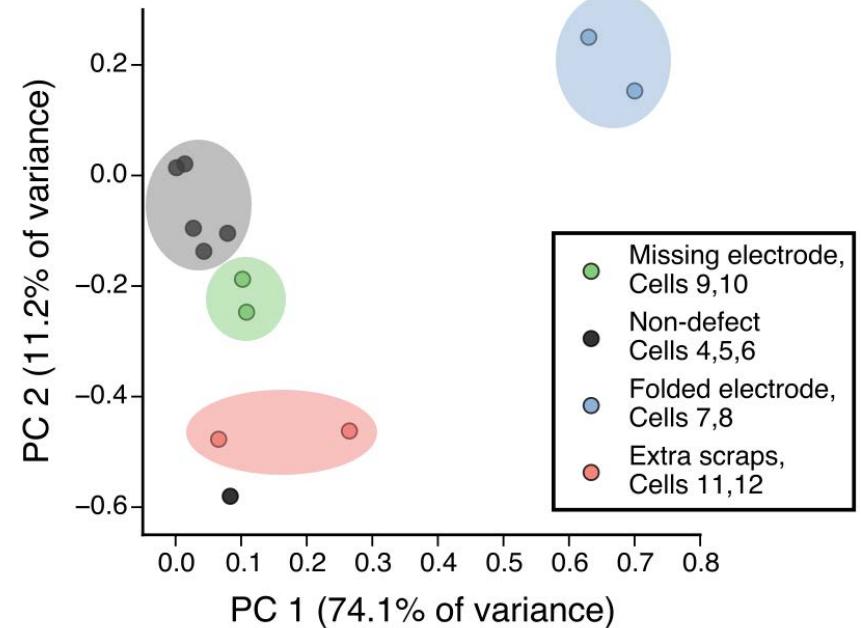
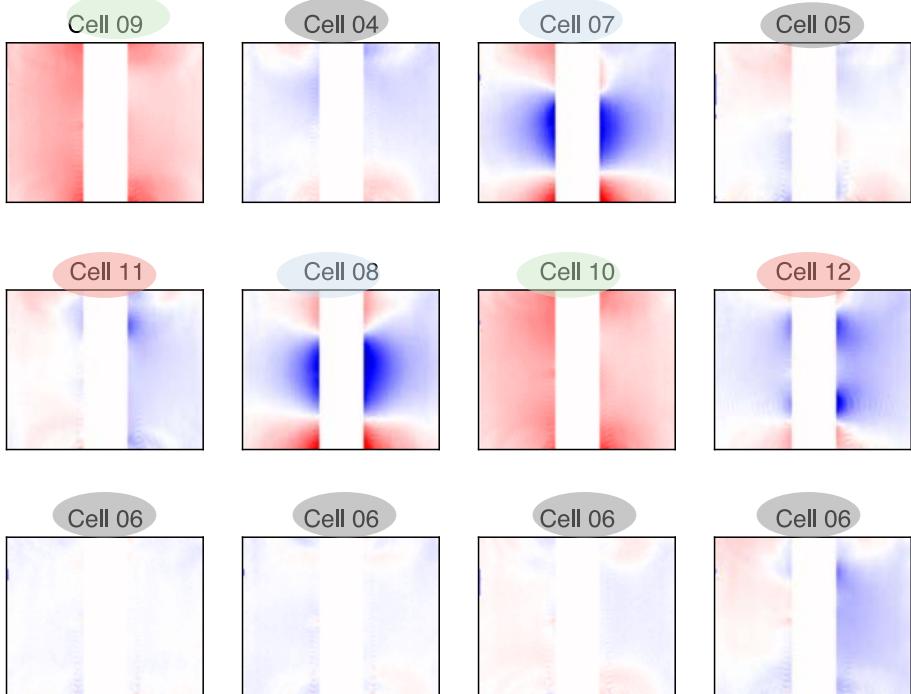


MISSING
ELECTRODE

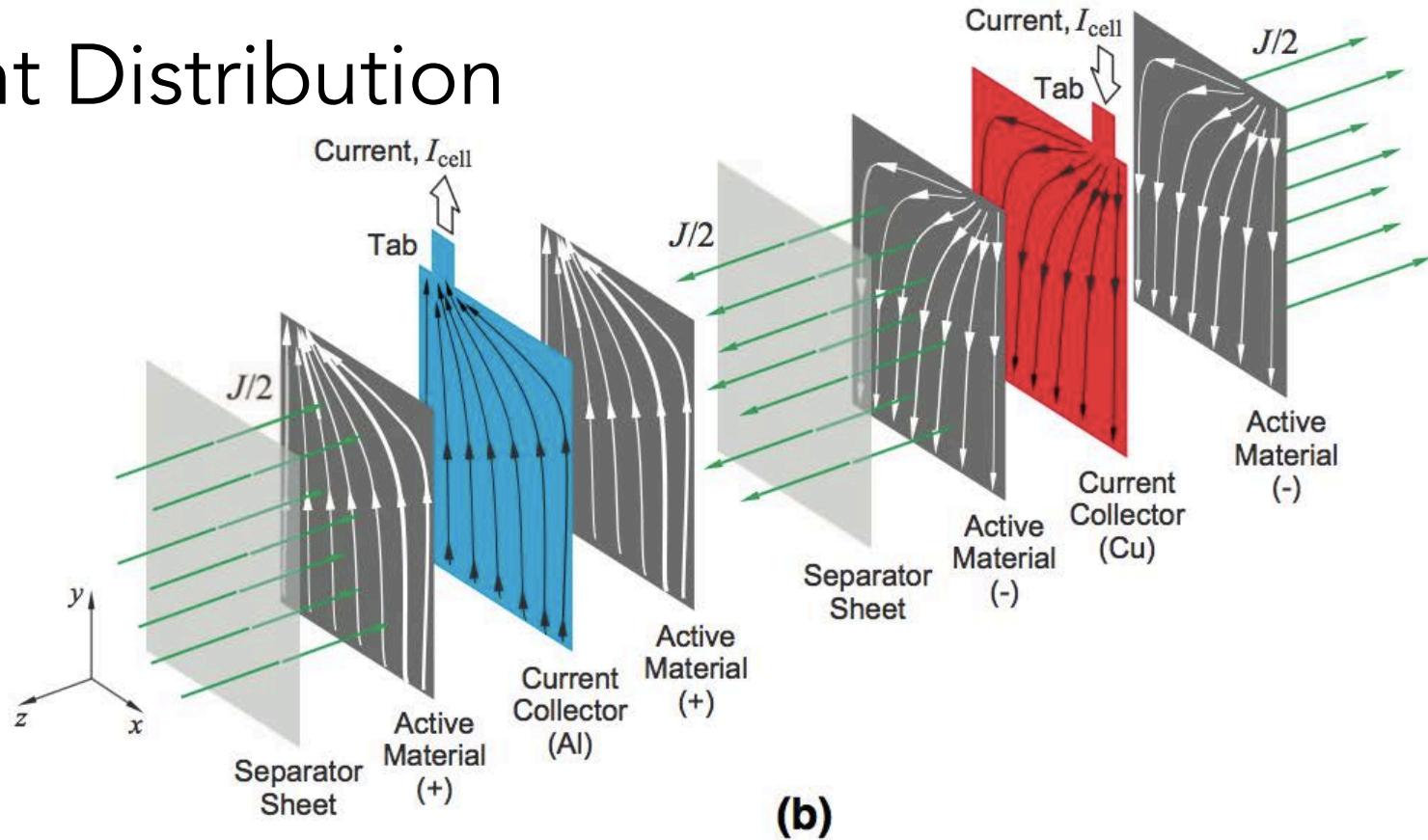
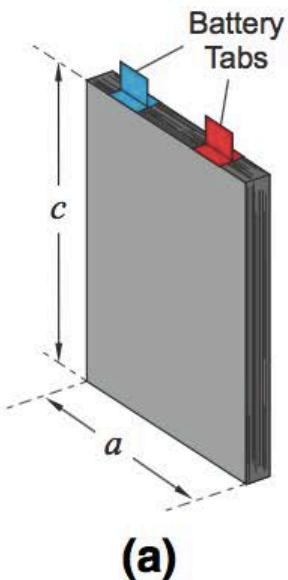


EXTRA SCRAPS



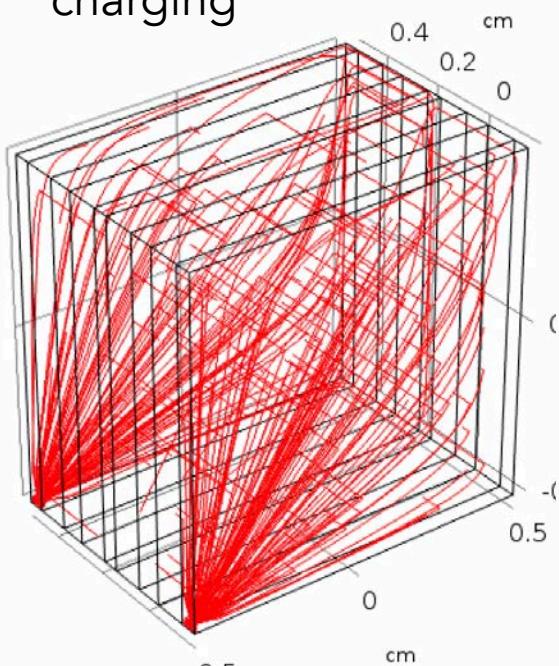


Current Distribution

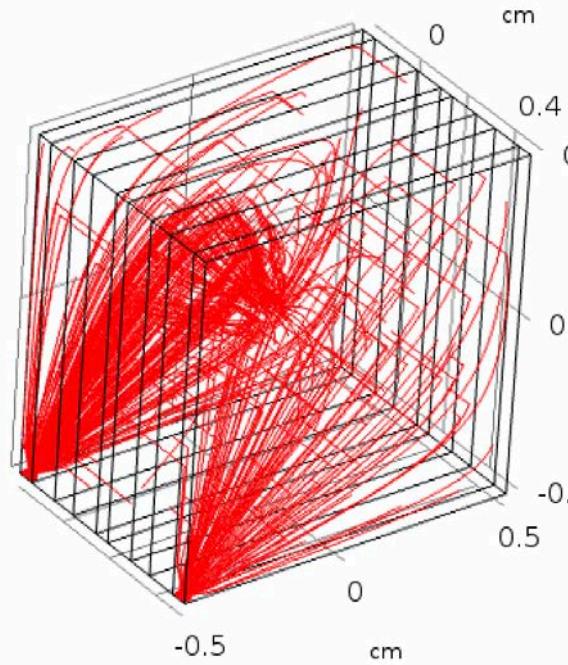


Current distributions

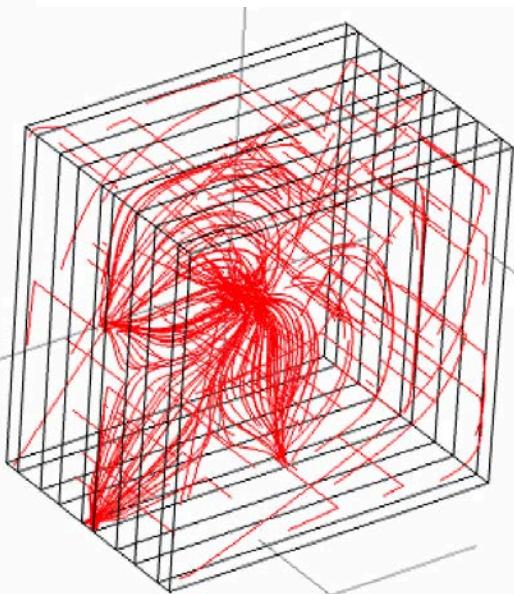
charging



charging; short

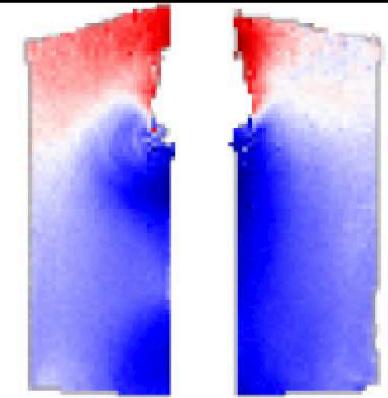


discharging; short



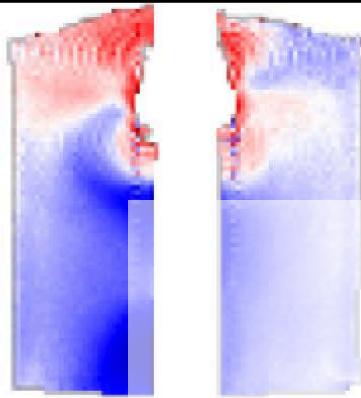
Current distributions with MRI

-125.00 mAh

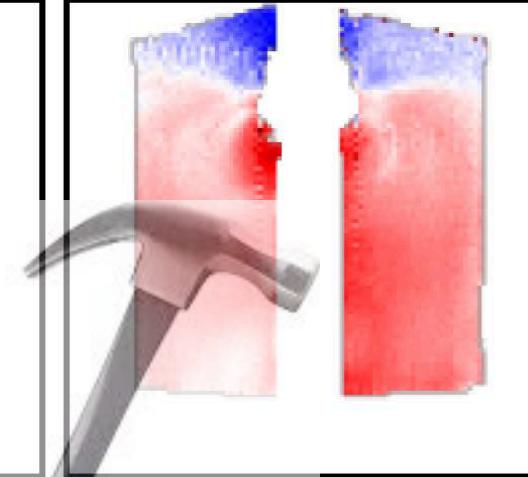


discharge

0.00 mAh



125.00 mAh



charge

0.75

0.00

-0.75

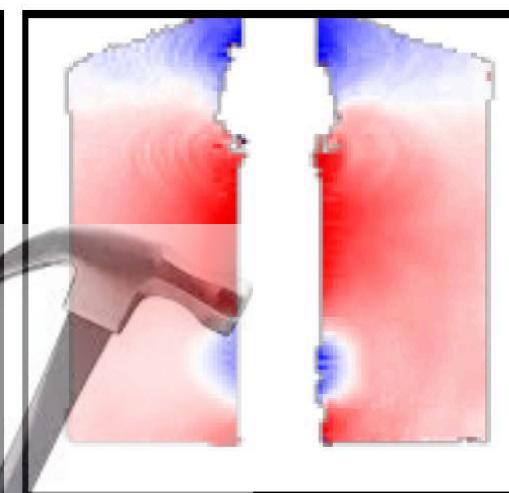
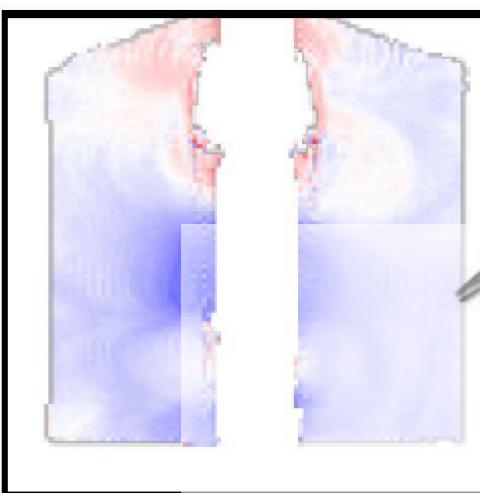
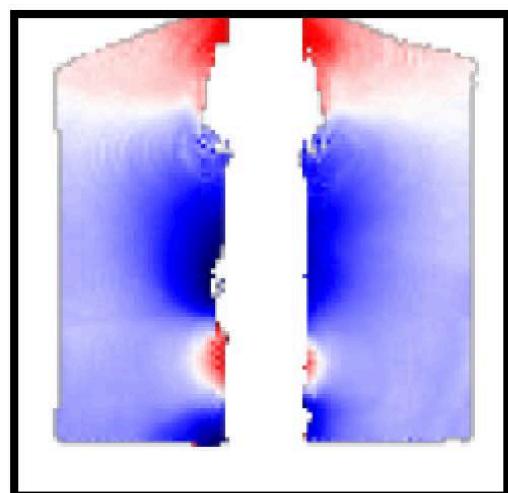
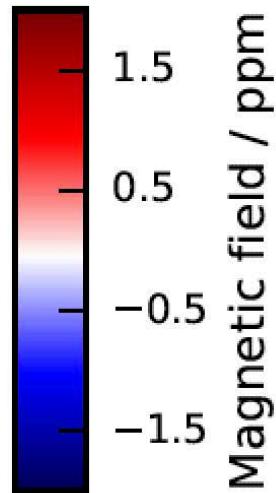
Magnetic field / ppm

Current distributions with MRI

-100.00 mAh

0.00 mAh

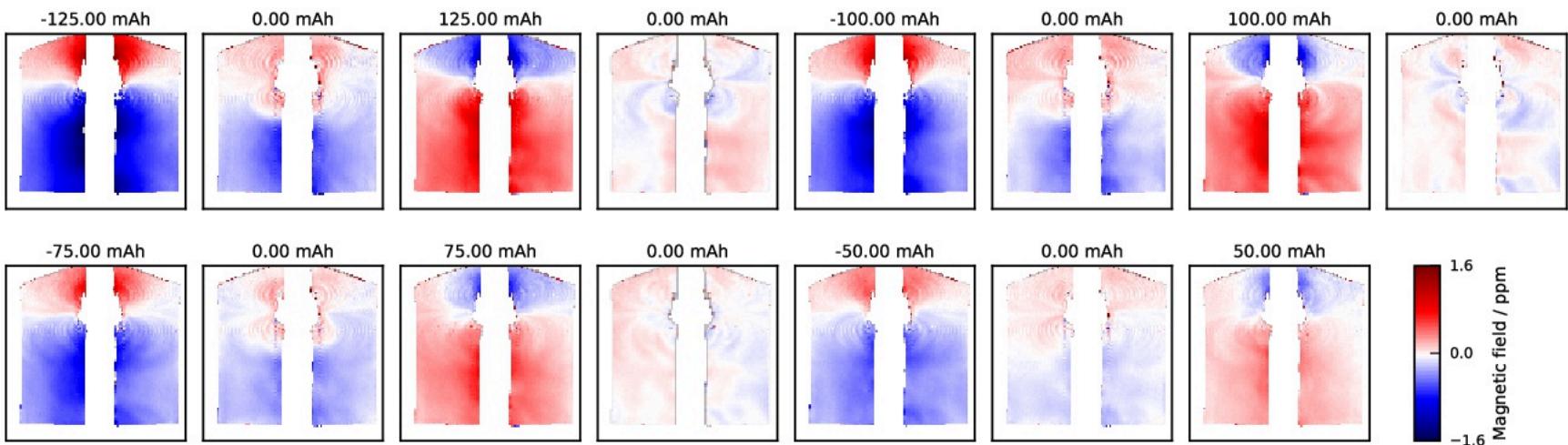
100.00 mAh

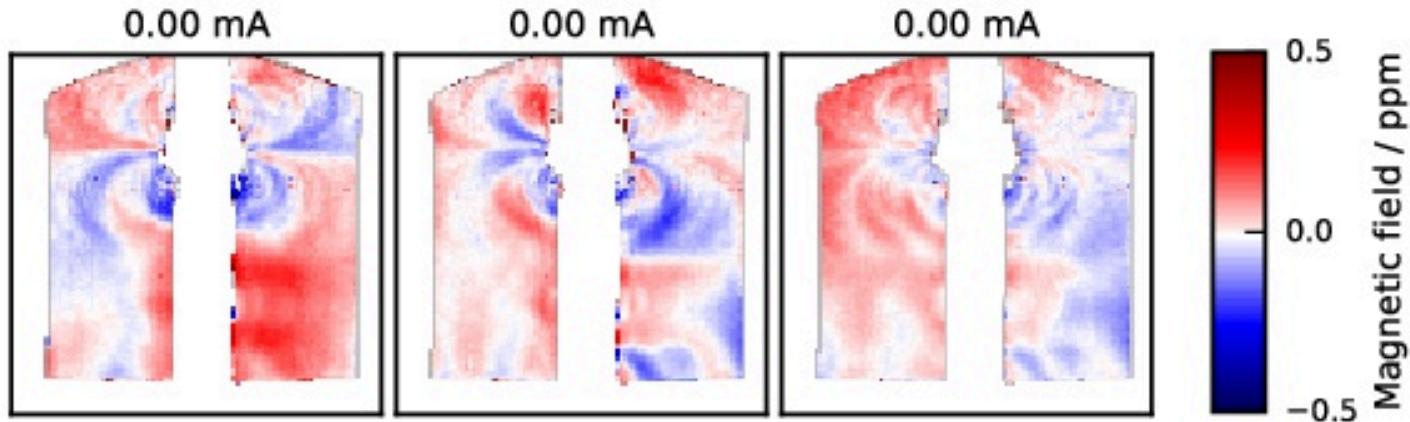


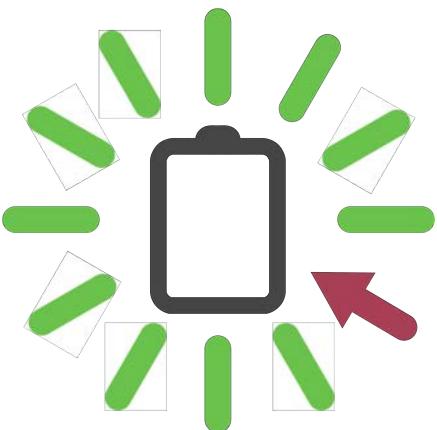
discharge



charge



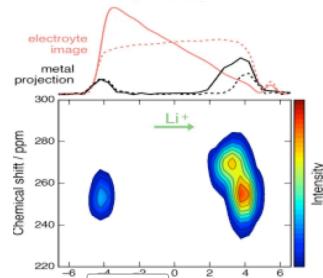




In-situ (operando) NMR/MRI

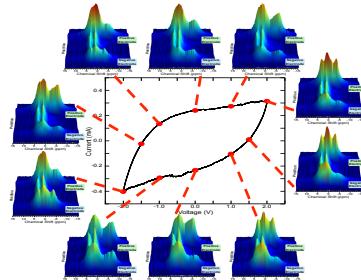
Li-dendrite visualization

- ${}^7\text{Li}$ MRI / CSI
- ${}^1\text{H}$ MRI



Supercapacitors

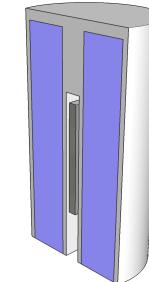
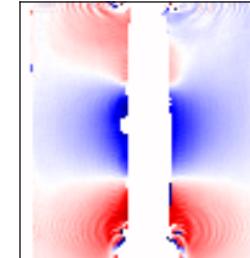
- ${}^1\text{H}$ / ${}^{11}\text{B}$ MRI



"In real life" Inside-out MRI

Commercial-type cell analysis

- SOC
- SOH
- Current distribution



Relevant Publications

- S. Chandrashekhar, N. M. Trease, H. J. Chang, L.-S. Du, C. P. Grey, A. Jerschow, *⁷Li MRI of Li batteries reveals location of microstructural lithium*, Nature Mater., 11, 311-315, 2012, <http://www.nature.com/doifinder/10.1038/nmat3246>.
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