PDF Analysis of Batteries Using Diffraction Computed Tomography

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REsource Centre for X-rays

RECX

Norwegian Centre for X-ray Diffraction, Scattering and Imaging

Thanks!

- Jonas Sottmann
- Amund Ruud
- Øystein Fjellvåg
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- Gavin Vaughan
- Marco Di Michiel

UiO University of Oslo

Forskningsrådet

Energy Storage

- Renewable Energy requires efficient energy storage!
- Batteries are a key part of this…

Sodium vs lithium

- Lithium batteries are commonplace in the modern world
- Solid state and Light weight ideal for mobile applications
- Well developed technology

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- Solid state and Light weight ideal for mobile applications
- Well developed technology
- Rare element, expensive!
- Sodium has similar chemistry
- Heavier but cheaper, and widely available!
- Potentially useful for stationary applications (e.g. home power storage)

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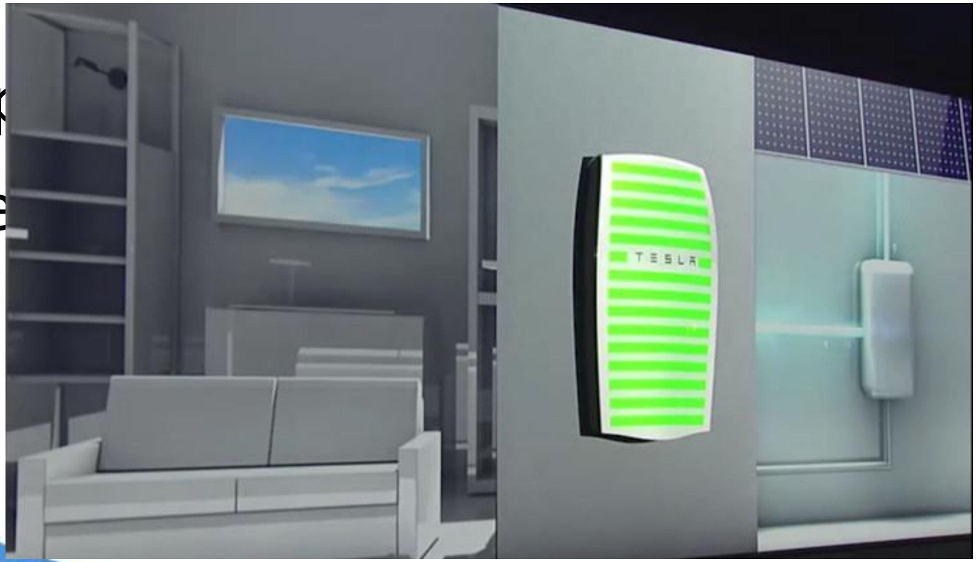
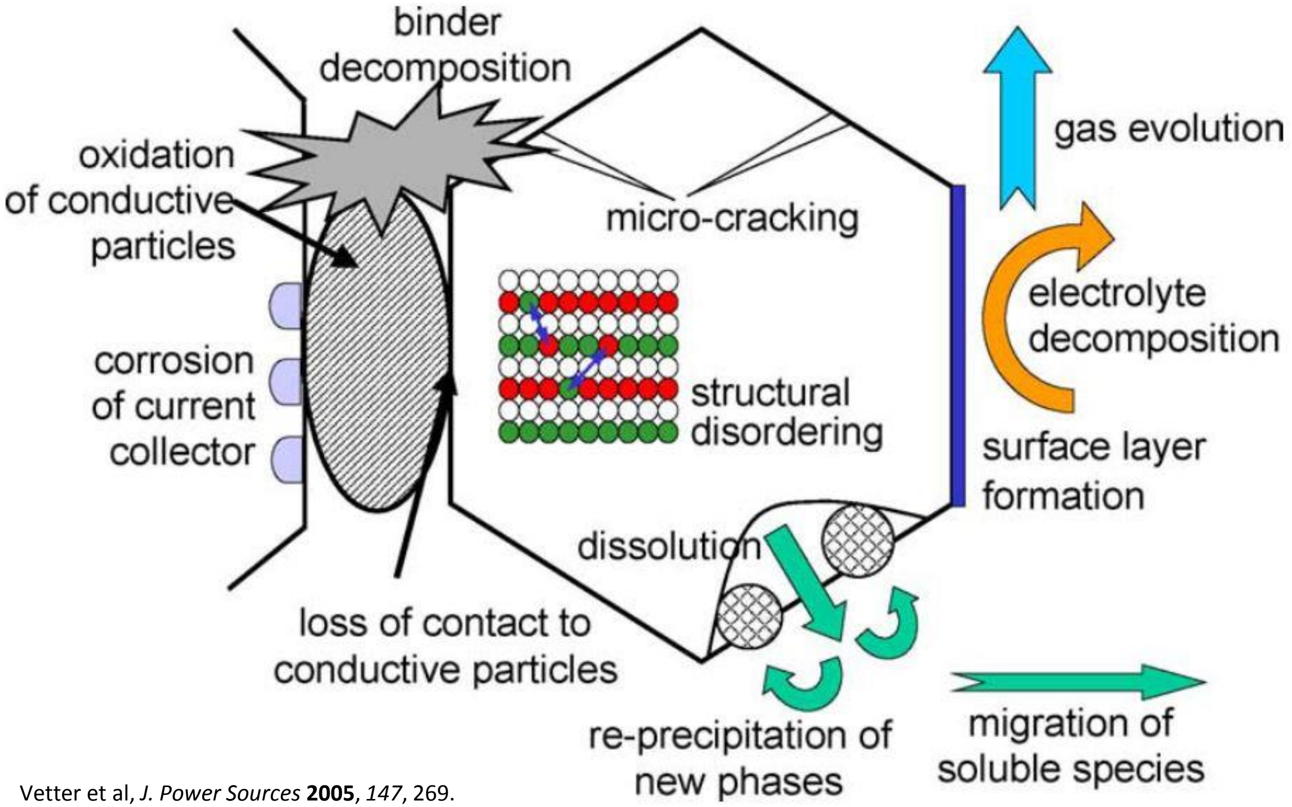


Degradation Mechanisms

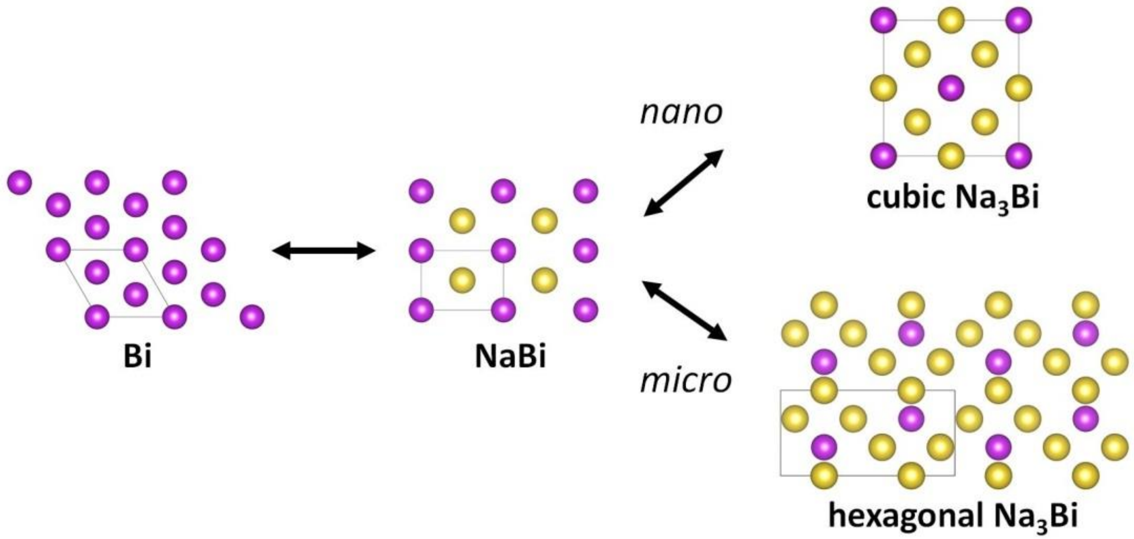


Vetter et al, *J. Power Sources* **2005**, *147*, 269.

Making Better Batteries

- Capacity, cycling stability, safety and cost are among the targets for improvement
- We have focussed on discovering and understanding new anode materials
- Nanosizing can be a useful method

Nano sizing in Bismuth



Sottmann et al, Chem
Mater 2016

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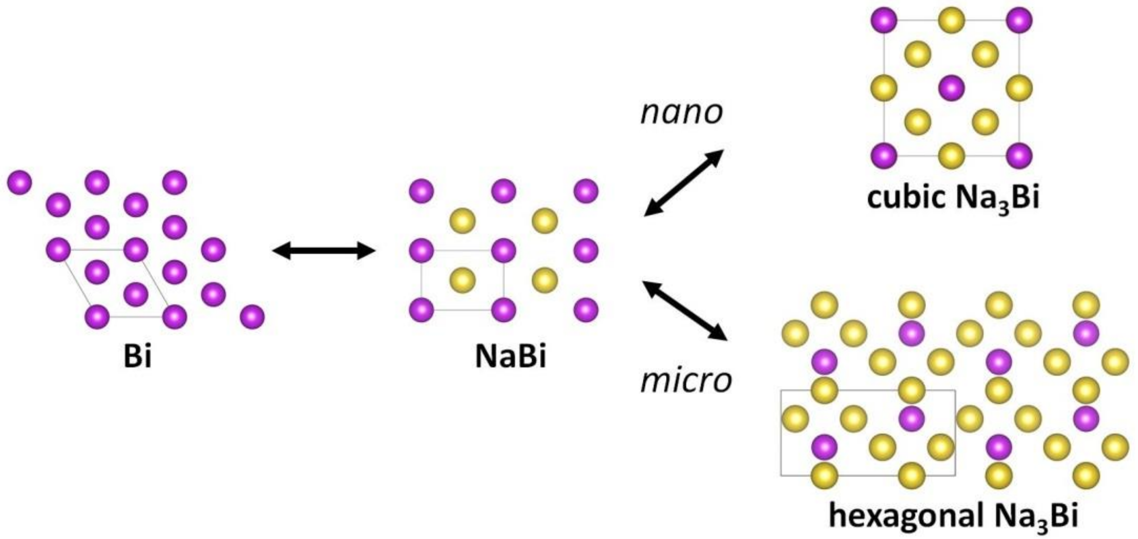
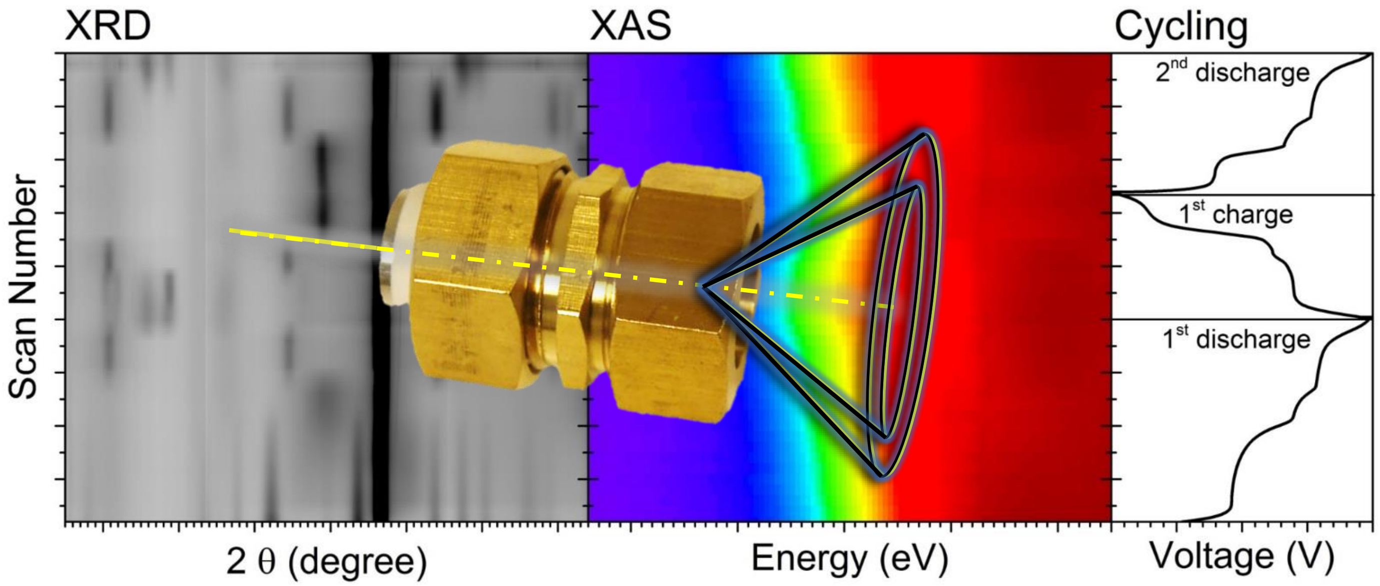


380 $mAhg^{-1}$ after 100 charge/discharge cycles

80 $mAhg^{-1}$ after 15 charge/discharge cycles

Sottmann et al, Chem Mater 2016

The trouble with *Operando* Characterization of batteries



Swiss-Norwegian Beam Lines at ESRF

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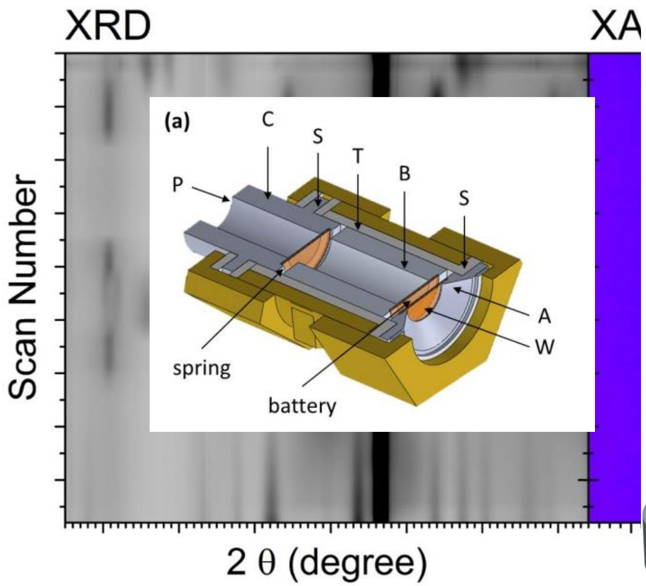

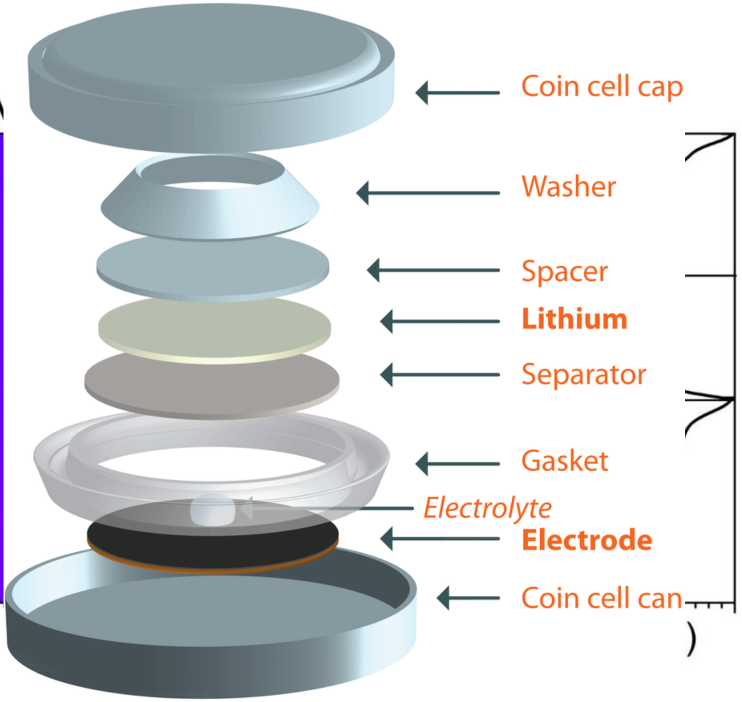

Swiss-Norwegian Beam Lines
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The Second Problem

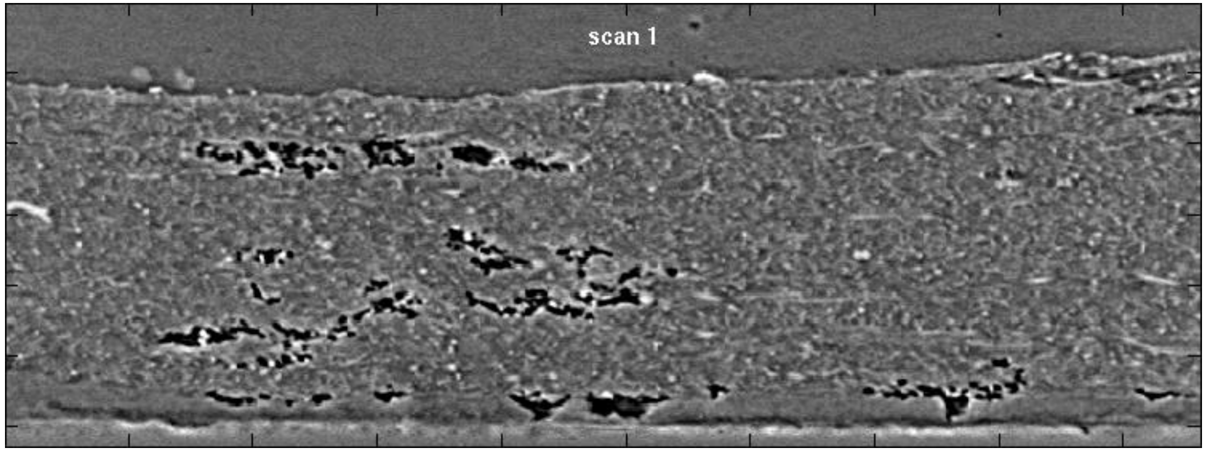
- Many interesting battery materials are amorphous
  - Methods based on crystal structure cannot be applied
- Total scattering methods can help

The Second Problem

- Many interesting battery materials are amorphous
  - Methods based on crystal structure cannot be applied
- Total scattering methods can help
  - But we must remove background and non-sample contributions

Computed Tomography (CT)

- Tomographic imaging allows us to visualise battery components
- This can be done in real time…



X-ray Diffraction-CT

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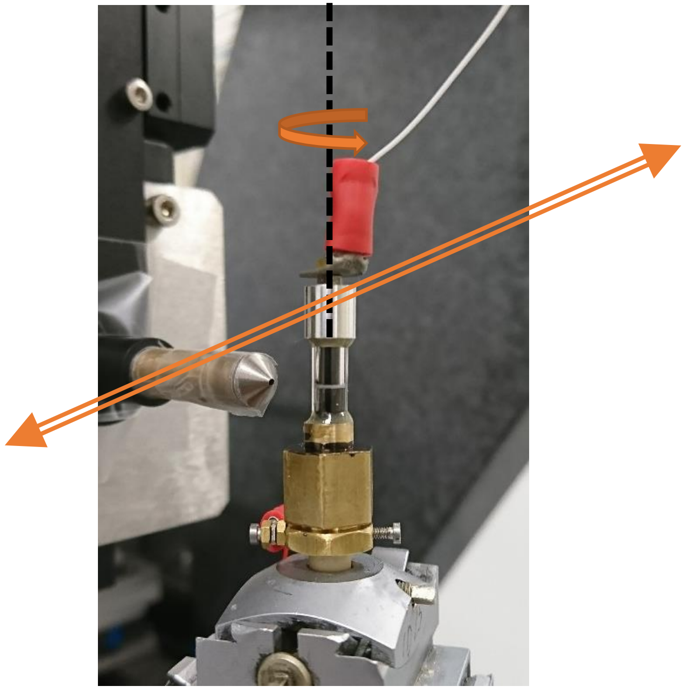

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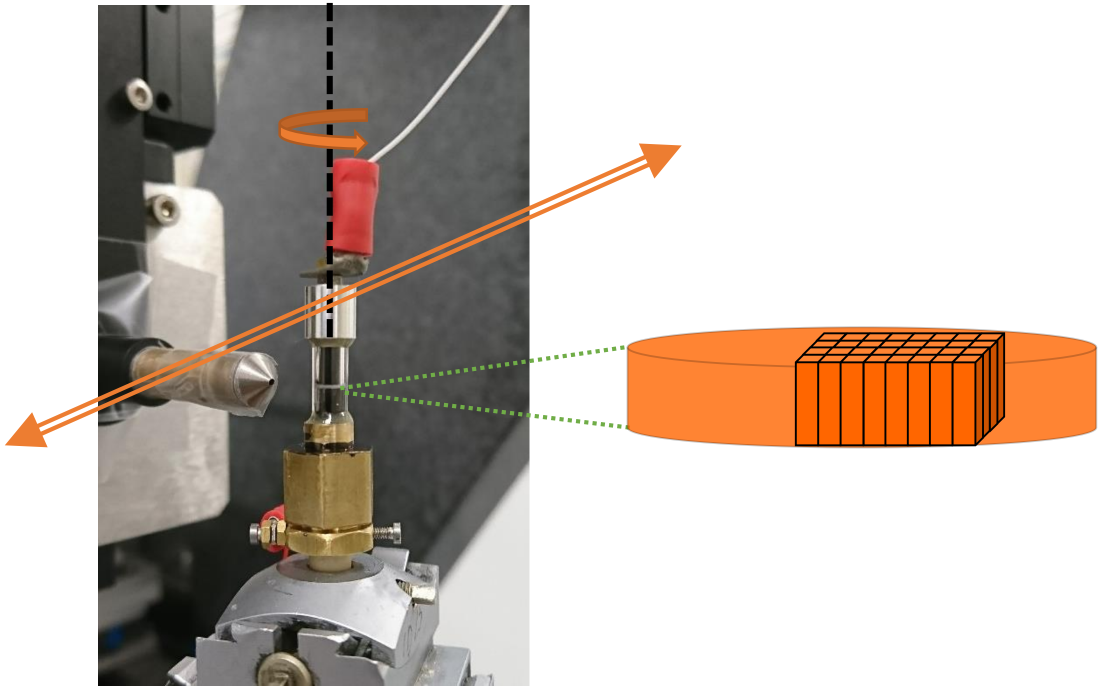

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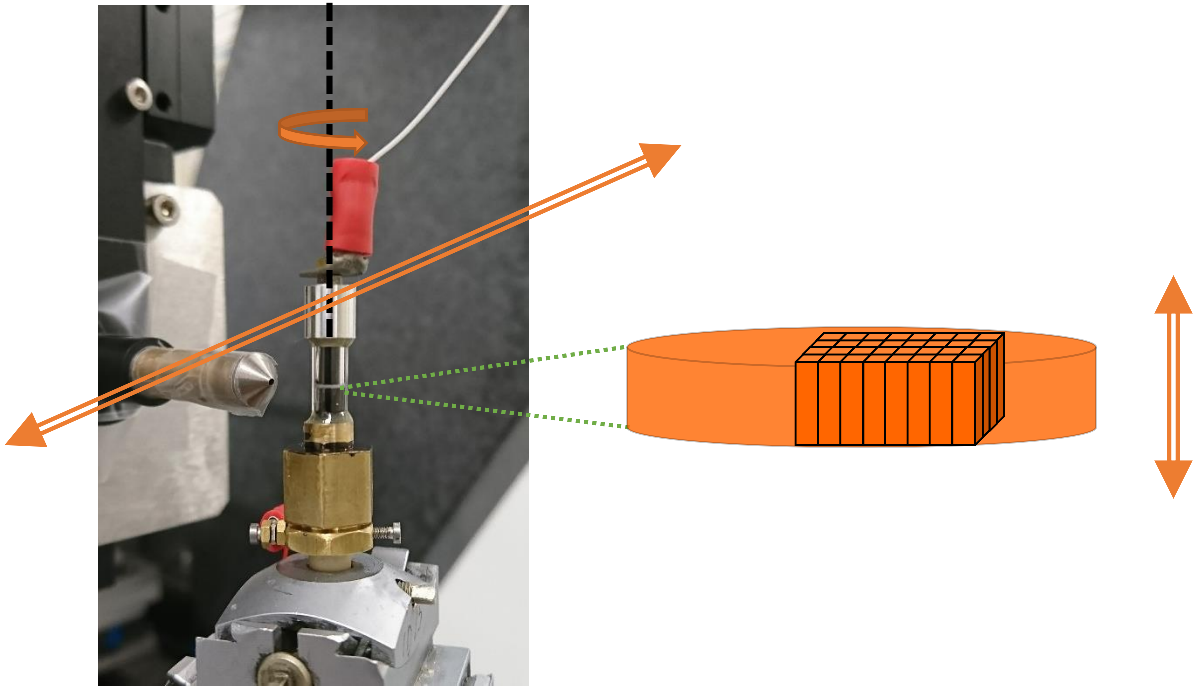
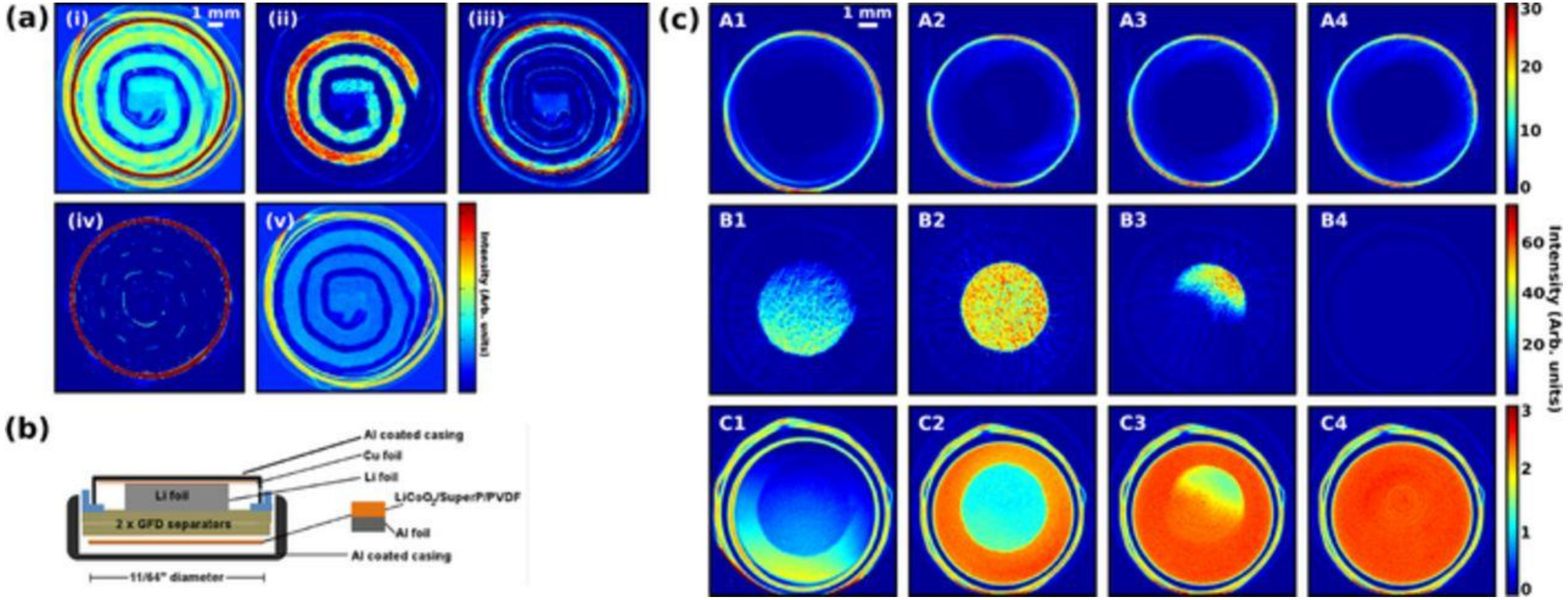


X-ray Diffraction-CT

- Recently computed tomography has been carried out using X-ray diffraction
- Initially basic analysis of Bragg peak intensities
- Full structural analysis of the data is possible using Rietveld and PDF methods

X-ray Diffraction-CT

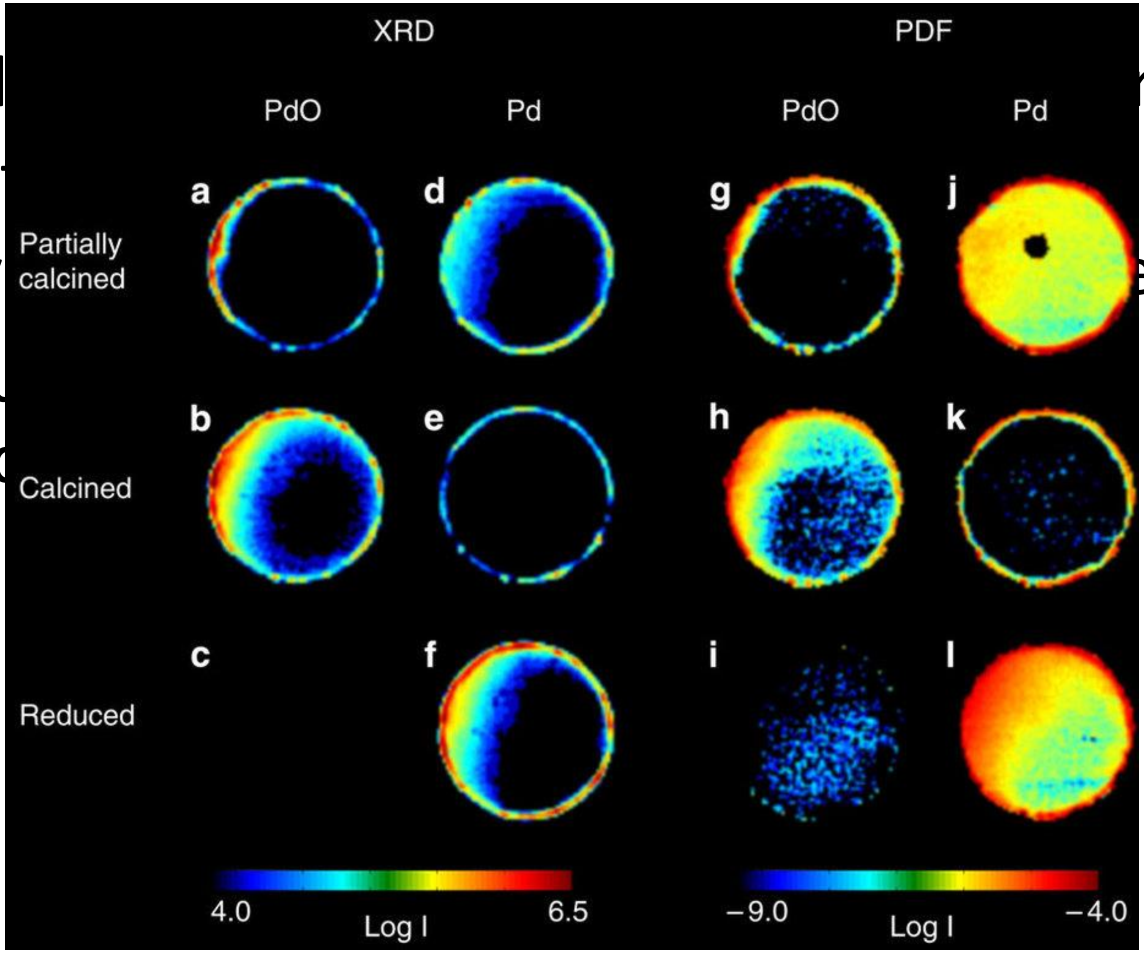
- Recently computed tomography has been carried out



Kirsten M. Ø. Jensen et al. J. Electrochem. Soc. 2015;162:A1310-A1314

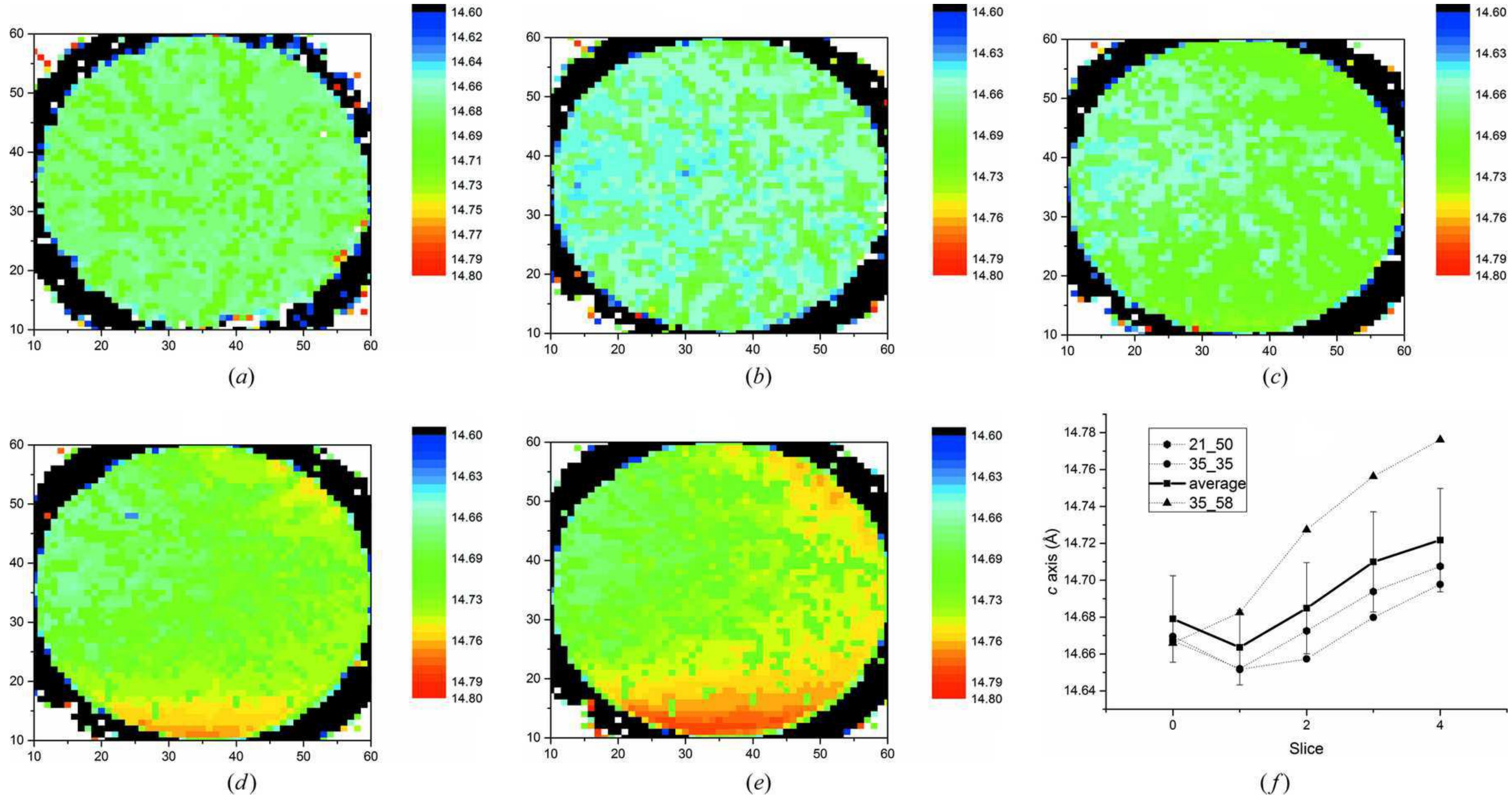
X-ray Diffraction-CT

- Recentl rried out using X-
- Initially es
- Full stru using Rietvelc



Jacques et al, Nature commun., 2013

X-ray Diffraction-CT

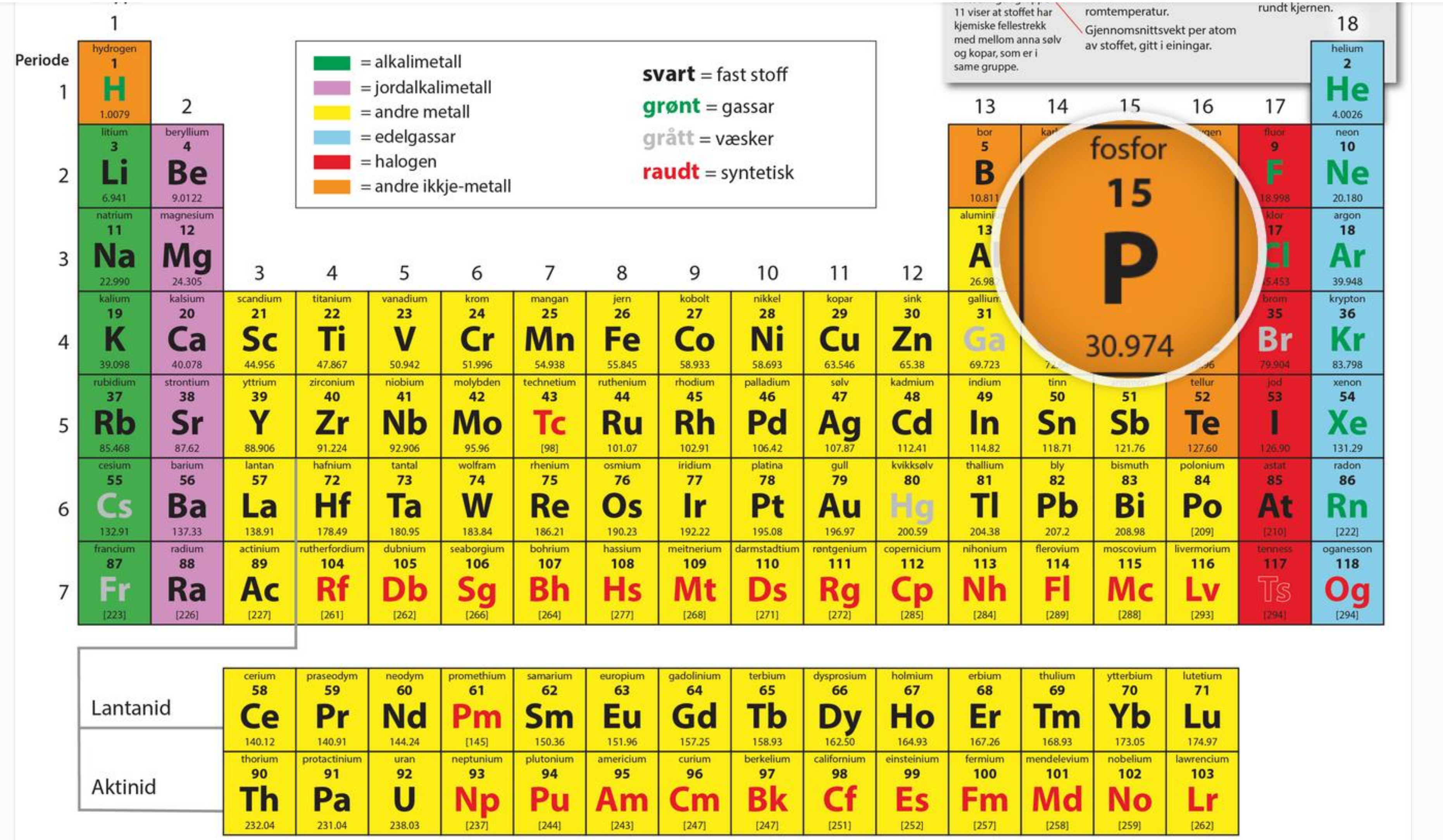


JAC Appl Cryst JOURNAL OF APPLIED CRYSTALLOGRAPHY

• **Wragg *et al.***

• **Volume 48** | **Part 6** | December 2015 | Pages 1719–1728 | 10.1107/S1600576715017288

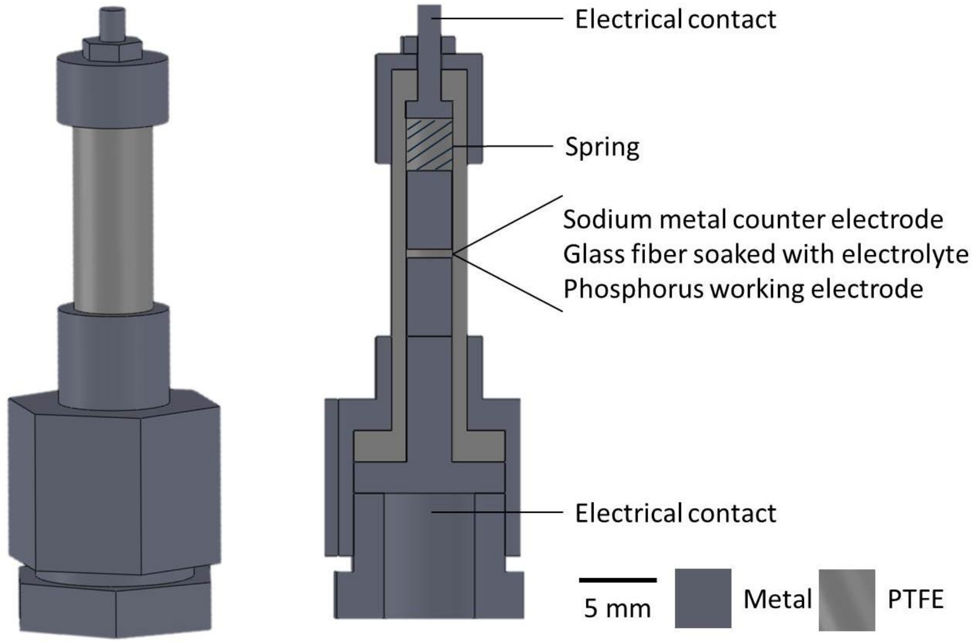
Phosphorus


11 viser at stoffet har kjemiske fellestrekk med mellom anna sølv og kopar, som er i same gruppe.
romtemperatur.
Gjennomsnittsvekt per atom av stoffet, gitt i einingar.
rundt kjernen.
Periode
= alkalimetall
= jordalkalimetall
= andre metall
= edelgassar
= halogen
= andre ikkje-metall
svart = fast stoff
grønt = gassar
grått = væsker
raudt = syntetisk
fosfor 15 P 30.974
hydrogen 1 H 1.0079
helium 2 He 4.0026
litium 3 Li 6.941
beryllium 4 Be 9.0122
bor 5 B 10.811
fluor 9 F 18.998
neon 10 Ne 20.180
natrium 11 Na 22.990
magnesium 12 Mg 24.305
argon 18 Ar 39.948
kalium 19 K 39.098
kalsium 20 Ca 40.078
scandium 21 Sc 44.956
titanium 22 Ti 47.867
vanadium 23 V 50.942
krom 24 Cr 51.996
mangan 25 Mn 54.938
jern 26 Fe 55.845
kobolt 27 Co 58.933
nikkel 28 Ni 58.693
kopar 29 Cu 63.546
sink 30 Zn 65.38
gallium 31 Ga 69.723
brom 35 Br 79.904
krypton 36 Kr 83.798
rubidium 37 Rb 85.468
strontium 38 Sr 87.62
yttrium 39 Y 88.906
zirconium 40 Zr 91.224
niobium 41 Nb 92.906
molybden 42 Mo 95.96
technetium 43 Tc [98]
ruthenium 44 Ru 101.07
rhodium 45 Rh 102.91
palladium 46 Pd 106.42
sølv 47 Ag 107.87
kadmium 48 Cd 112.41
indium 49 In 114.82
tinn 50 Sn 118.71
51 Sb 121.76
tellur 52 Te 127.60
jod 53 I 126.90
xenon 54 Xe 131.29
cesium 55 Cs 132.91
barium 56 Ba 137.33
lantan 57 La 138.91
hafnium 72 Hf 178.49
tantal 73 Ta 180.95
wolfram 74 W 183.84
rhenium 75 Re 186.21
osmium 76 Os 190.23
iridium 77 Ir 192.22
platina 78 Pt 195.08
gull 79 Au 196.97
kvikksølv 80 Hg 200.59
thallium 81 Tl 204.38
bly 82 Pb 207.2
bismuth 83 Bi 208.98
polonium 84 Po [209]
astat 85 At [210]
radon 86 Rn [222]
francium 87 Fr [223]
radium 88 Ra [226]
actinium 89 Ac [227]
rutherfordium 104 Rf [261]
dubnium 105 Db [262]
seaborgium 106 Sg [266]
bohrium 107 Bh [264]
hassium 108 Hs [277]
meitnerium 109 Mt [268]
darmstadtium 110 Ds [271]
røntgenium 111 Rg [272]
copernicium 112 Cp [285]
nihonium 113 Nh [284]
flerovium 114 Fl [289]
moscovium 115 Mc [288]
livermorium 116 Lv [293]
tenness 117 Ts [294]
oganesson 118 Og [294]
Lantanid
cerium 58 Ce 140.12
praseodym 59 Pr 140.91
neodym 60 Nd 144.24
promethium 61 Pm [145]
samarium 62 Sm 150.36
europium 63 Eu 151.96
gadolinium 64 Gd 157.25
terbium 65 Tb 158.93
dysprosium 66 Dy 162.50
holmium 67 Ho 164.93
erbium 68 Er 167.26
thulium 69 Tm 168.93
ytterbium 70 Yb 173.05
lutetium 71 Lu 174.97
Aktinid
thorium 90 Th 232.04
protactinium 91 Pa 231.04
uran 92 U 238.03
neptunium 93 Np [237]
plutonium 94 Pu [244]
americium 95 Am [243]
curium 96 Cm [247]
berkelium 97 Bk [247]
californium 98 Cf [251]
einsteinium 99 Es [252]
fermium 100 Fm [257]
mendelevium 101 Md [258]
nobelium 102 No [259]
lawrencium 103 Lr [262]

Phosphorus

- High capacity anode for sodium ion batteries
  - Each P can alloy 3 Na-ions
  - Lowest molecular mass
- Only one of the compounds formed during cycling is crystalline
- Low X-ray scattering power
- The mechanism of cycling has remained obscure despite *post mortem* XRD, NMR and TEM studies
- No *operando* structural studies

Battery XRD-CT Cell
Targeting specific components



Battery XRD-CT Cell
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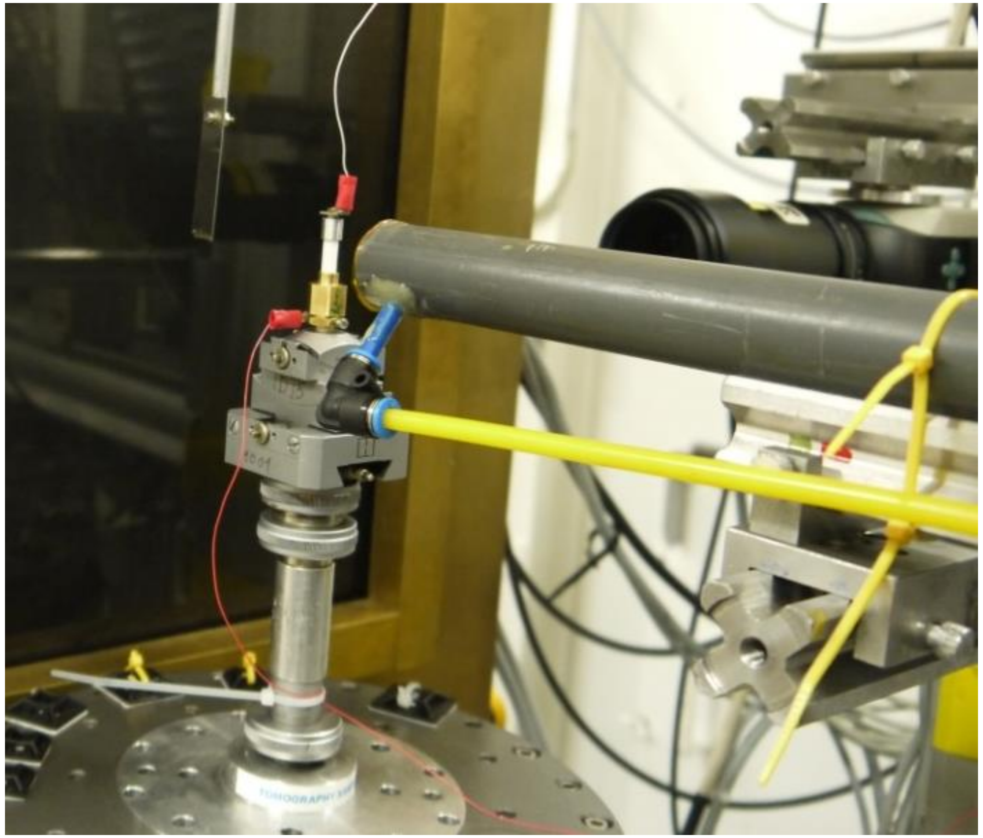
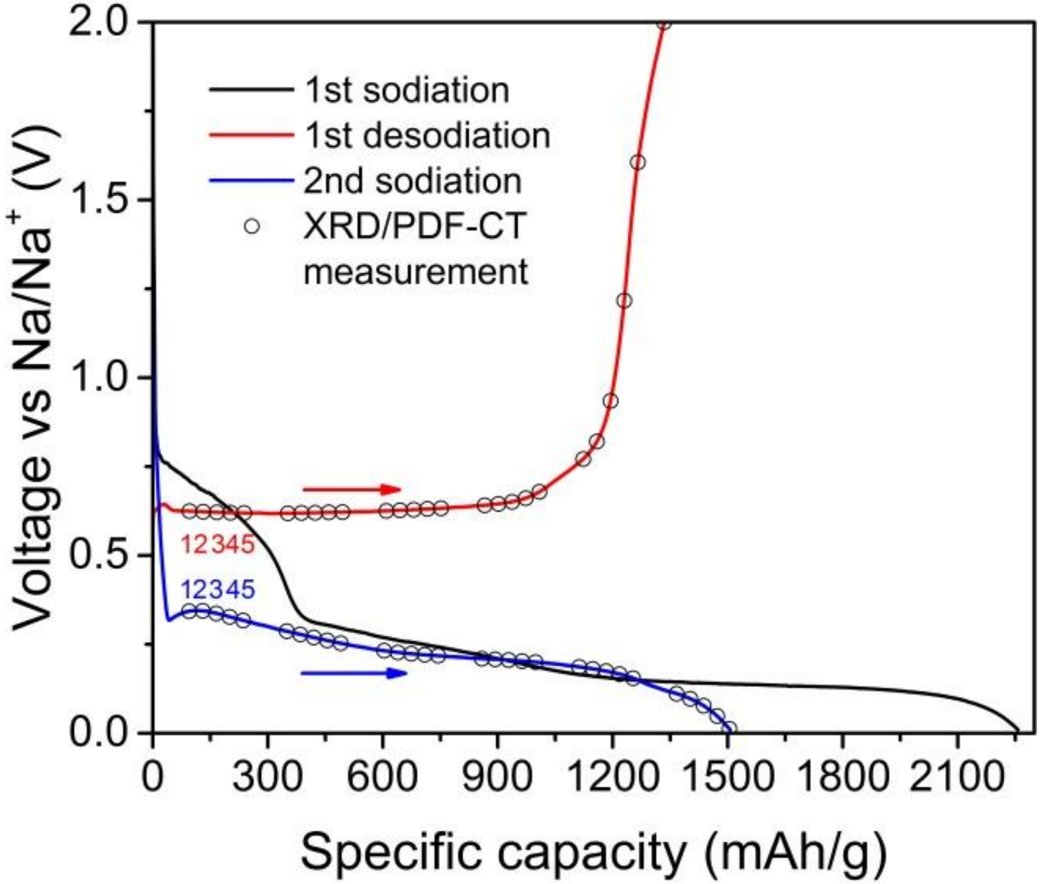
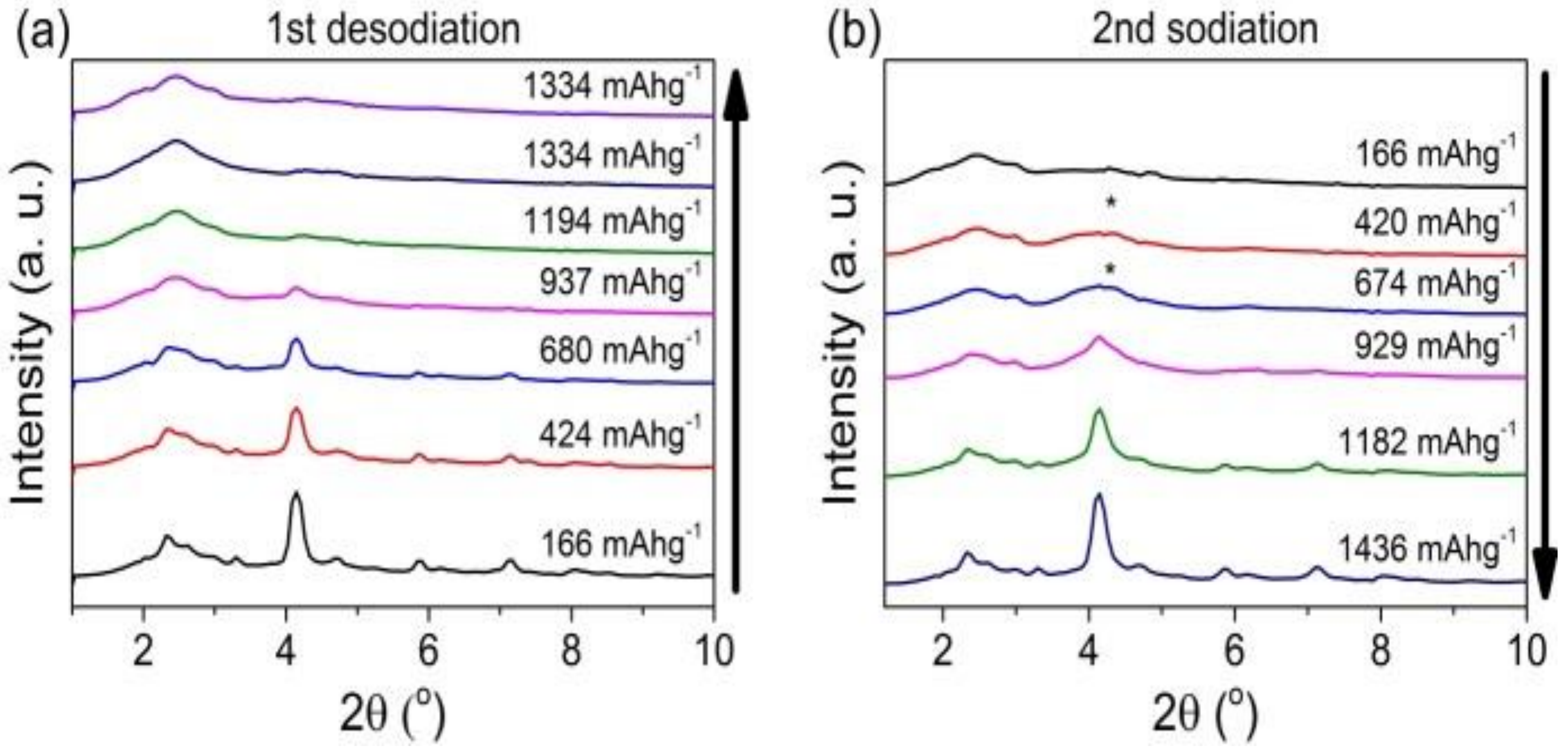


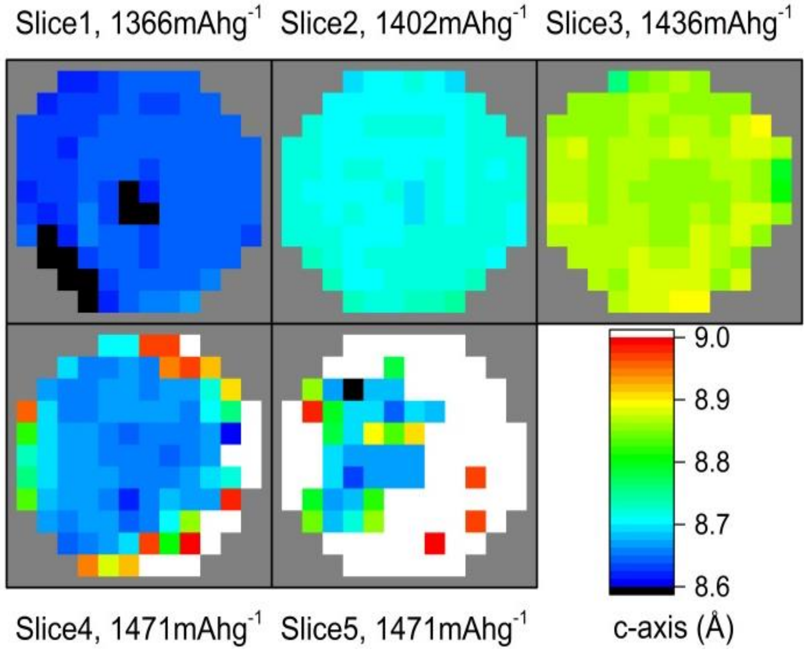
Results- cycling



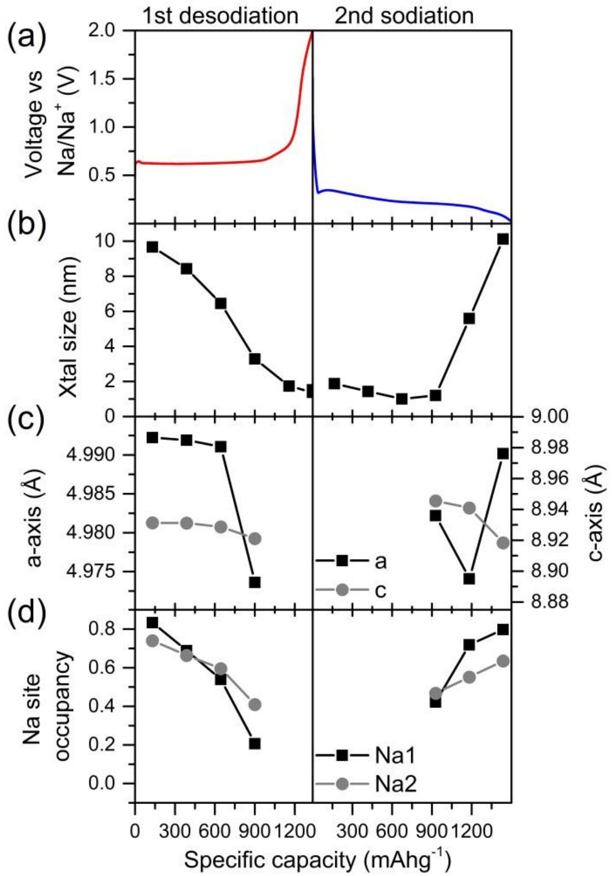
Results- XRD


(a)
1st desodiation
1334 mAhg-1
1334 mAhg-1
1194 mAhg-1
937 mAhg-1
680 mAhg-1
424 mAhg-1
166 mAhg-1
Intensity (a. u.)
2
4
6
8
10
2θ (°)
(b)
2nd sodiation
166 mAhg-1
420 mAhg-1
674 mAhg-1
929 mAhg-1
1182 mAhg-1
1436 mAhg-1
Intensity (a. u.)
2
4
6
8
10
2θ (°)

Results- XRD



Slice1, 1366mAhg-1
Slice2, 1402mAhg-1
Slice3, 1436mAhg-1
Slice4, 1471mAhg-1
Slice5, 1471mAhg-1
9.0
8.9
8.8
8.7
8.6
c-axis (Å)

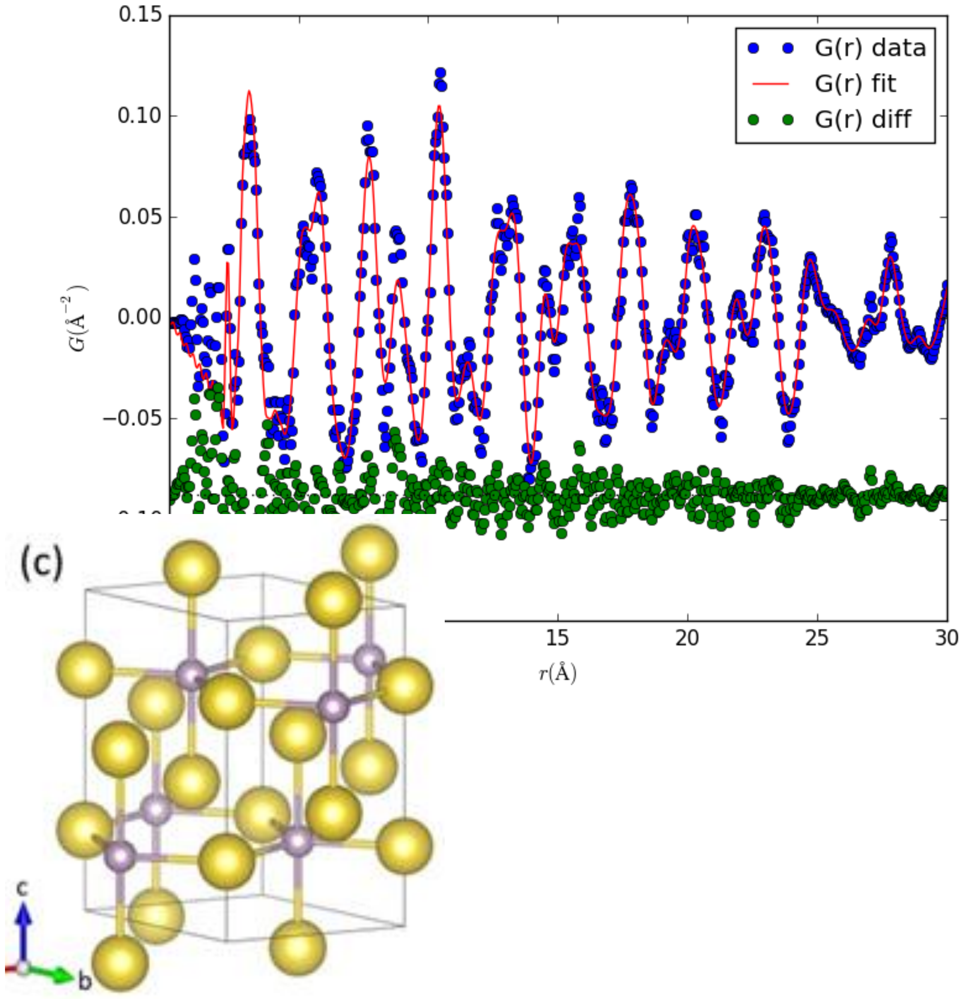


1st desodiation
2nd sodiation
(a)
Voltage vs Na/Na+ (V)
(b)
Xtal size (nm)
(c)
a-axis (Å)
c-axis (Å)
a
c
(d)
Na site occupancy
Na1
Na2
Specific capacity (mAhg-1)

PDF fitting

- PDF data quality was poor…
- Data summed over all voxels of each tomogram
- Spline fit used to reduce noise before data conversion
- PDFfit command line
  - Clusters and crystalline structures in same refinement

PDF- Desodiation



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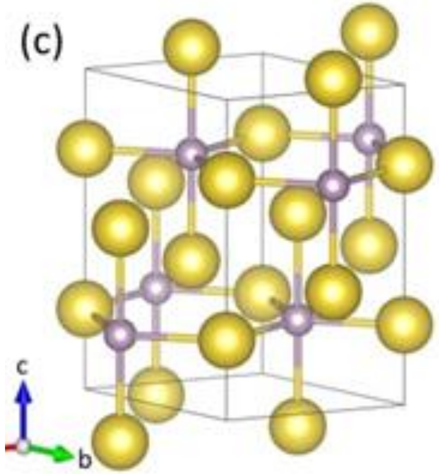
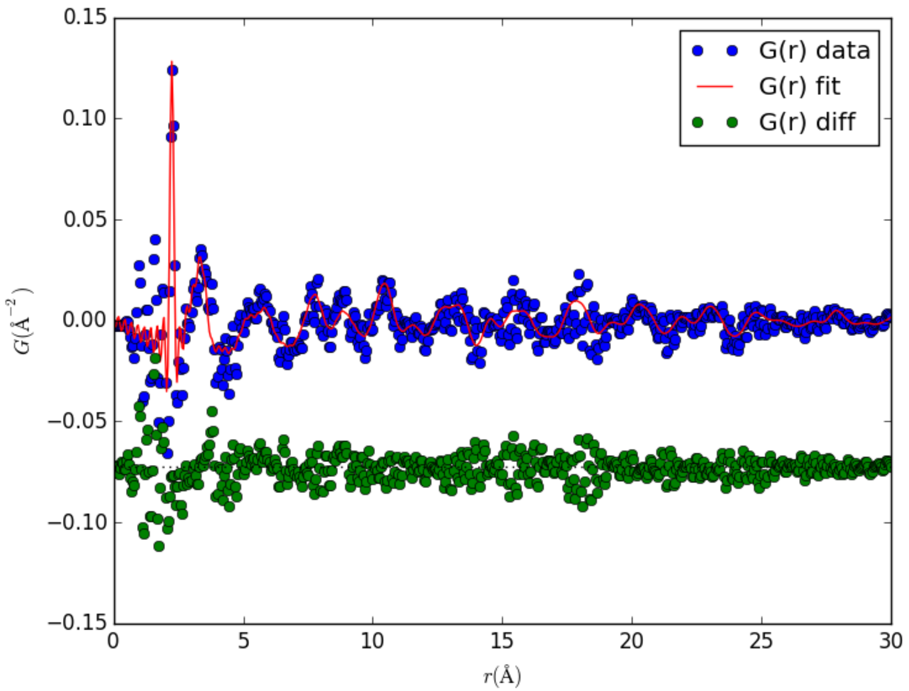
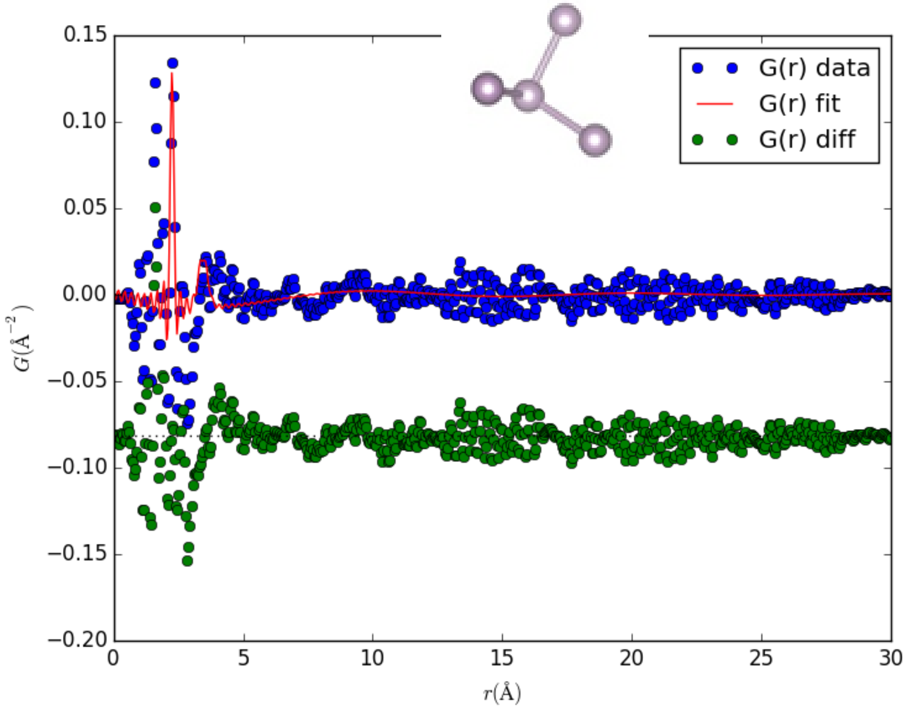
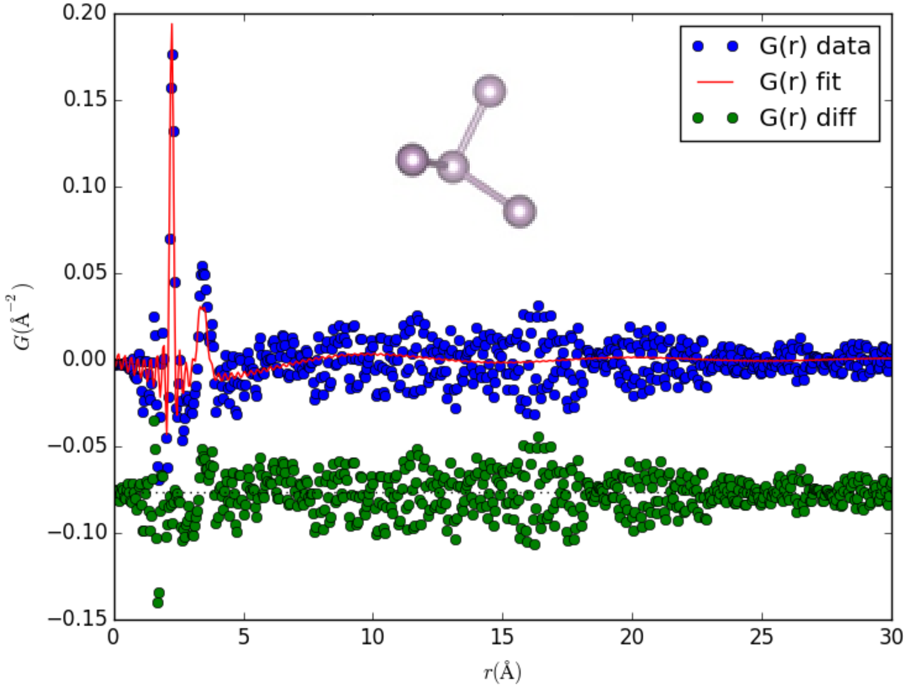




PDF- Desodiation



PDF - Sodiation



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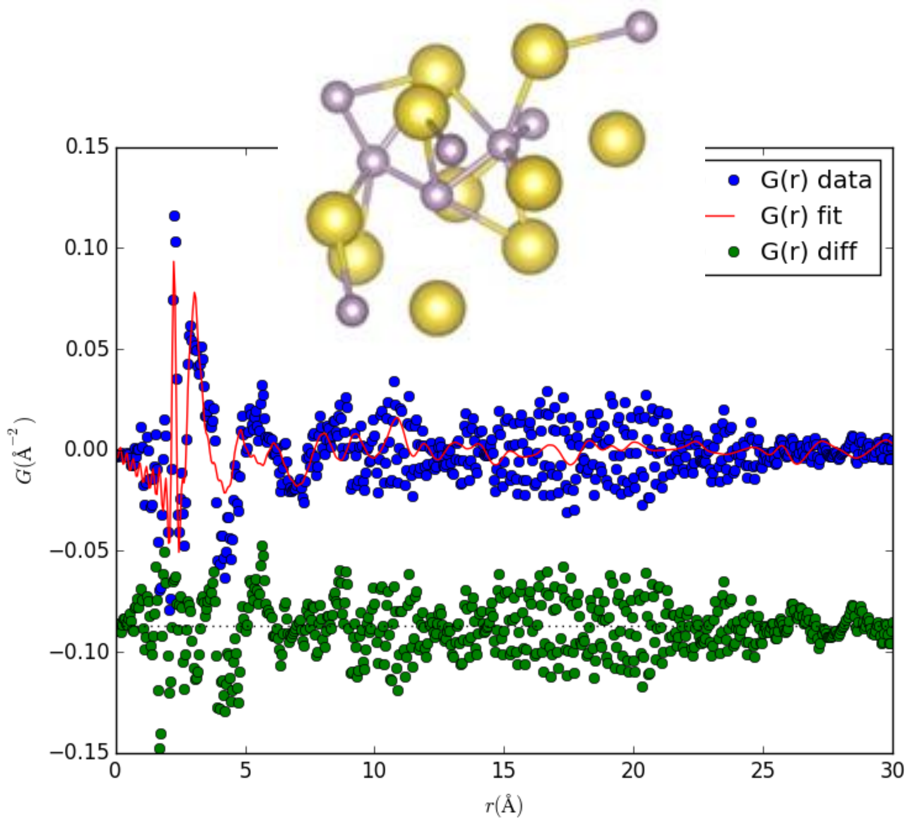

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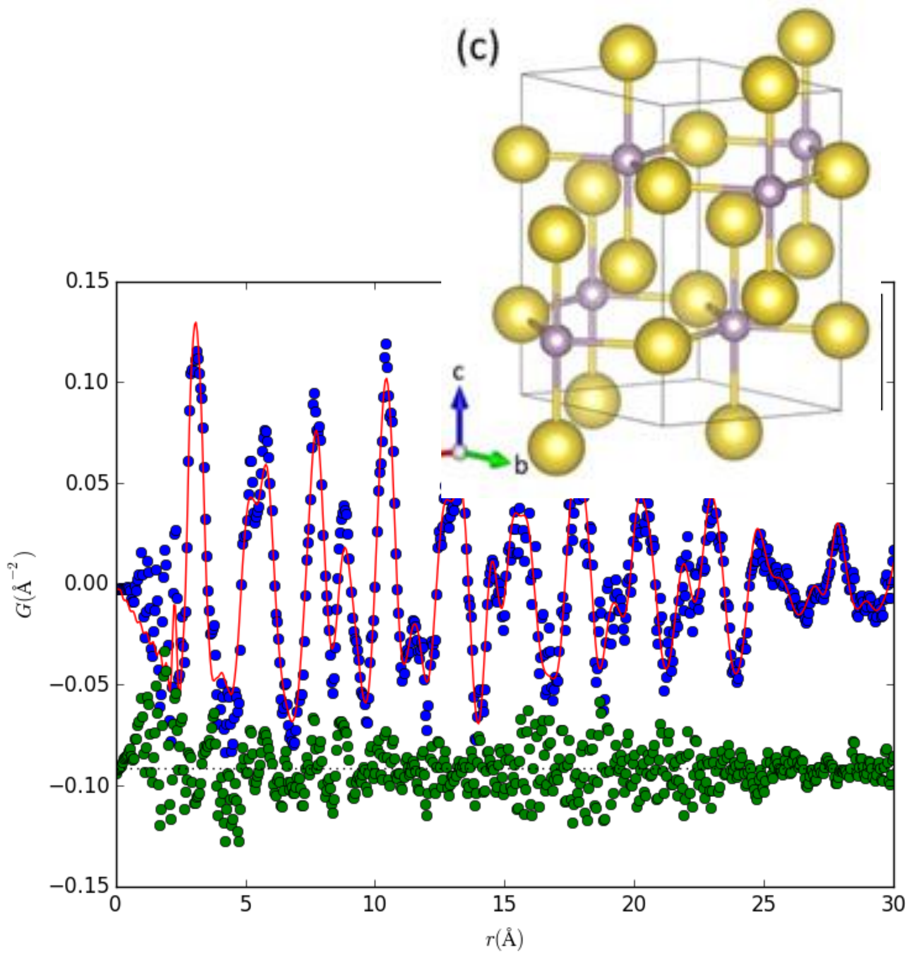
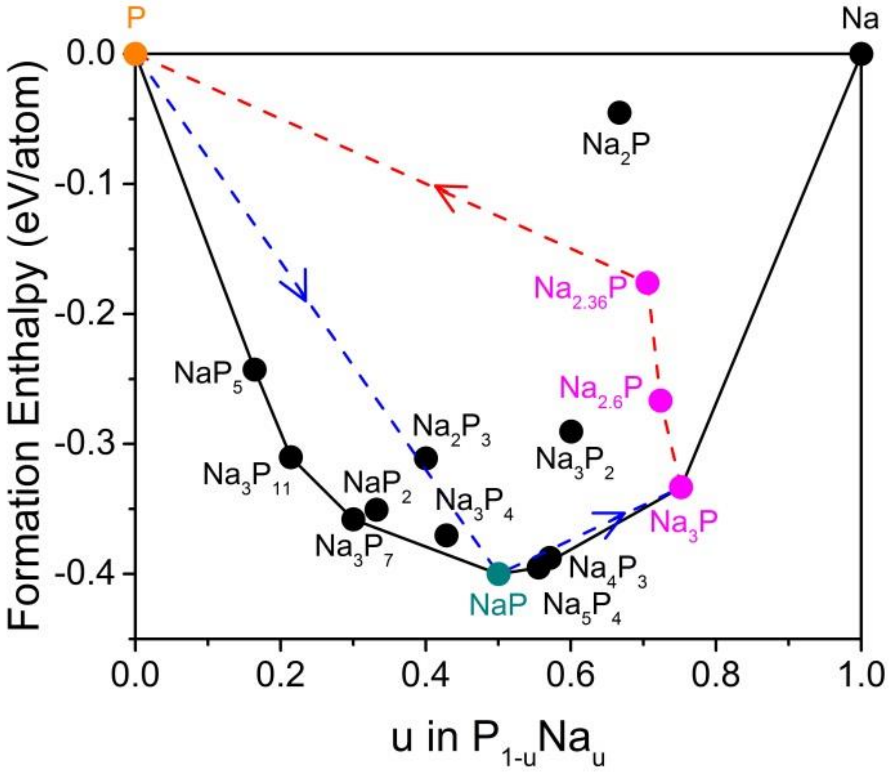


Calculations and Conclusions



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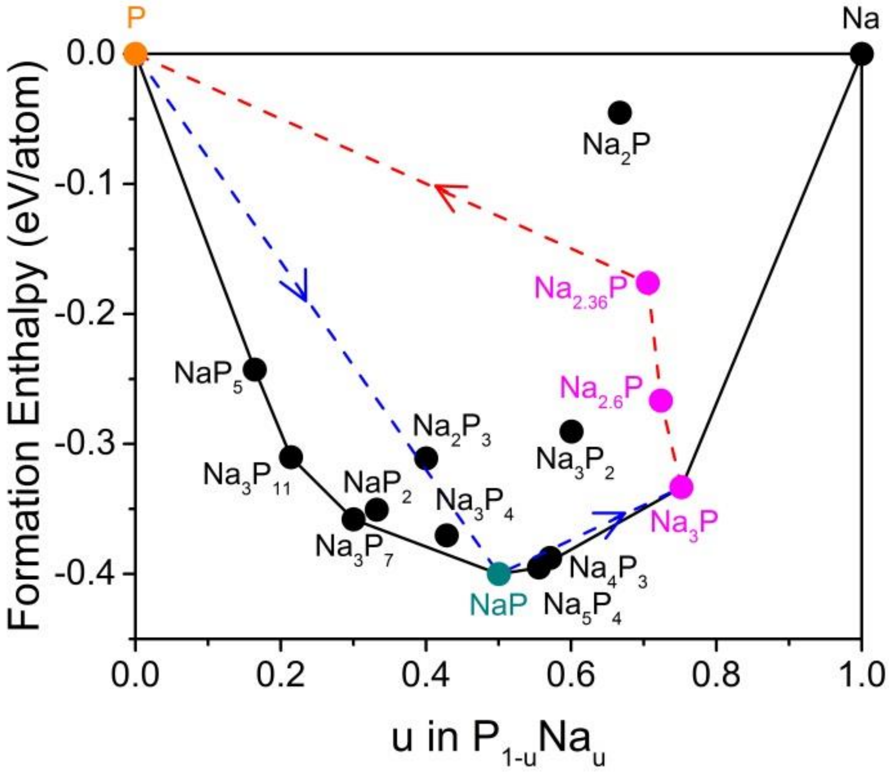

- Sodiation = thermodynamic (P – NaP- Na_3P)
- Desodiation = kinetic (deintercalation from $Na_{3-x}P$)
- PDF-CT can be used to get better information from specific components- averaging across the whole tomogram

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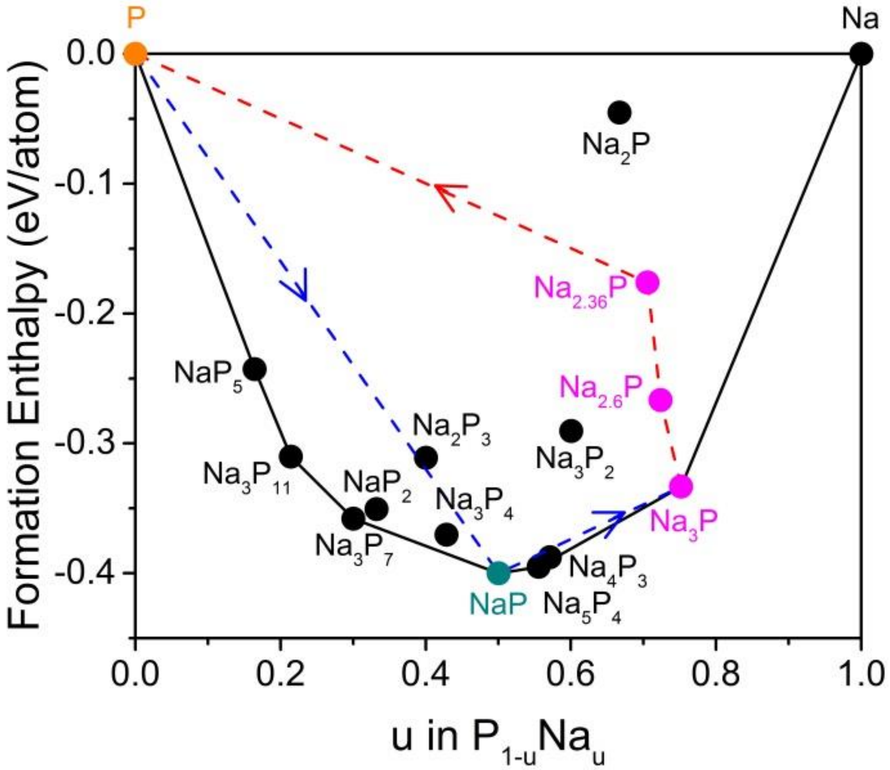

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- PDF-CT can be used to get better information from specific components- averaging across the whole tomogram
- Can we get better PDF data for structure analysis **and** mapping?

Bismuth Metallates revisited

- Excellent cycling properties
  - High capacity
  - Capacity is retained over many cycles

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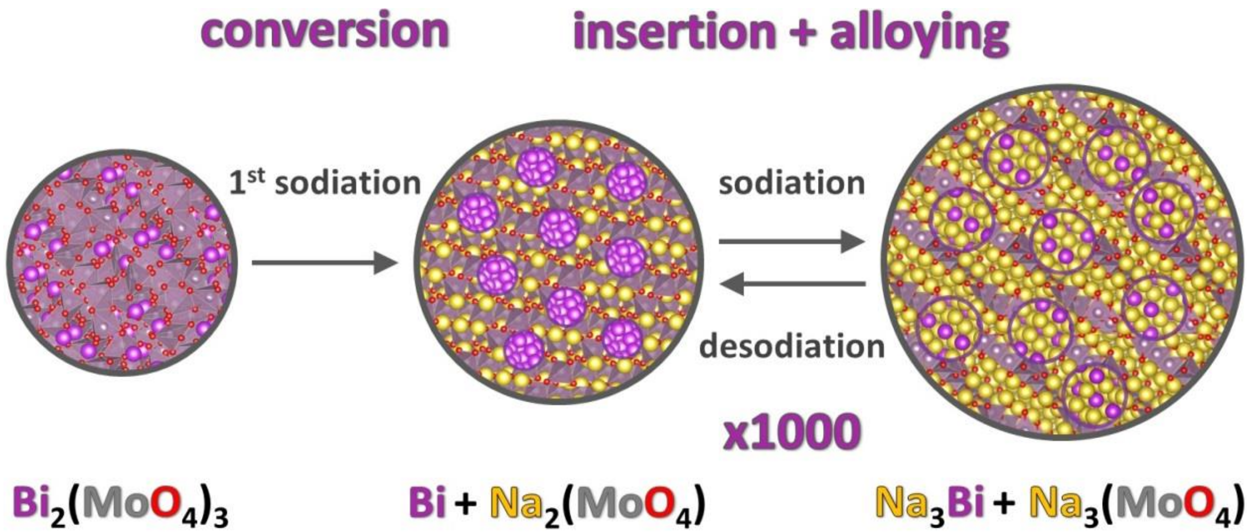
Sottmann et al, Chem. Mater, 2017



Bismuth Metallates revisited

- Excellent cycling properties
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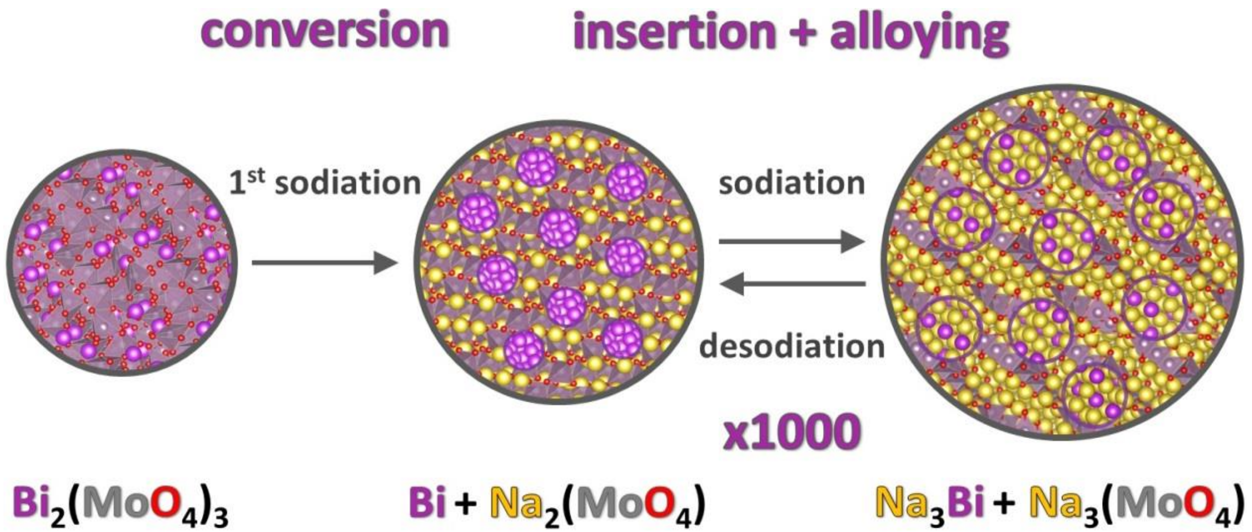
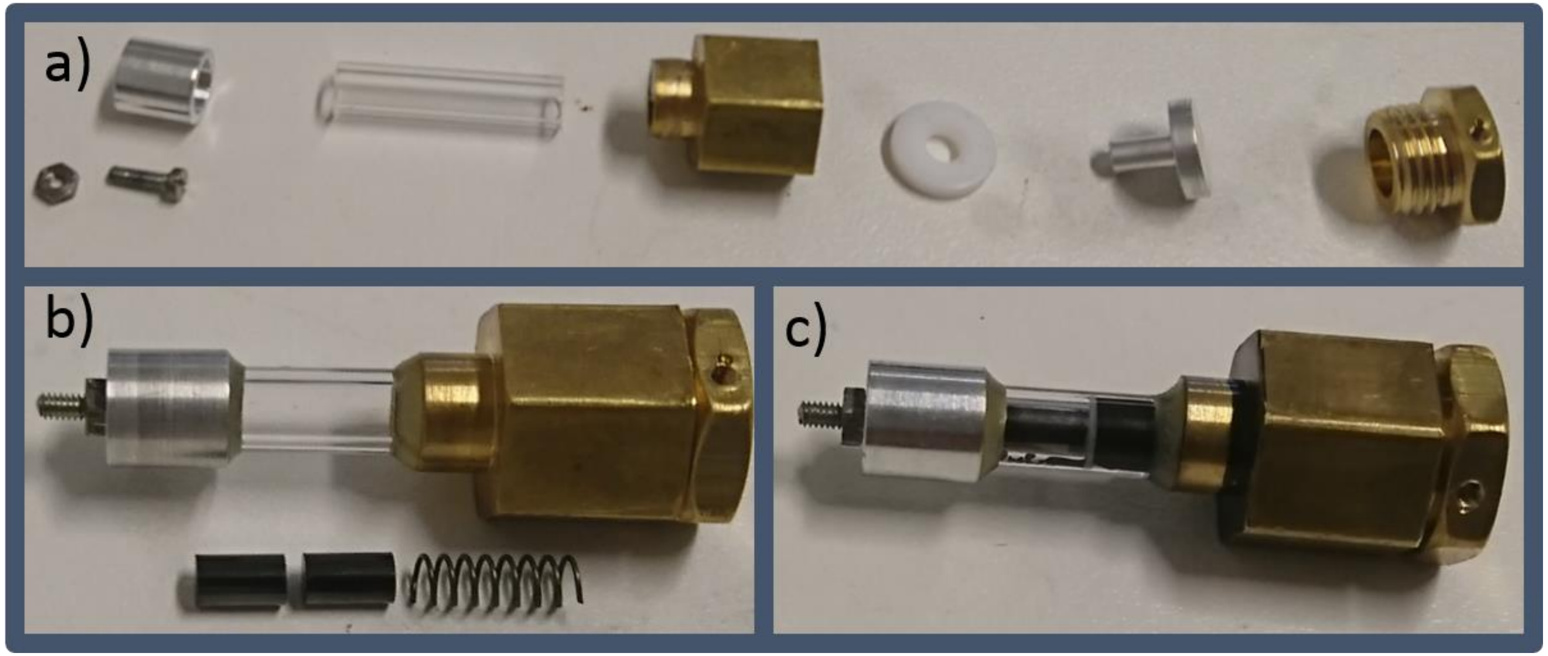
- We belived this was due to nanostructure
  - Coating of bismuth nanoparticles with vanadate/molybdate

Sottmann et al, Chem. Mater, 2017



Improved tomo cell and ID15 Upgrade



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