Understanding physical and chemical properties of energy storage materials with synchrotron radiation

Enrique G. Michel
Universidad Autónoma de Madrid, Spain

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Universidad Autónoma de Madrid
Departamento de Física de la Materia Condensada
IfiMAC Condensed Matter Physics Center
EXCELENCIA MARÍA DE MAEZTU

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Summary

Introduction to Li ion and Na ion batteries: why Li and Na?

$LiCoO_2$ cathode: delithiation process and phase coexistence (ARPES, XPS and PEEM).

Solid-state batteries: learning about cathodes and mitigating degradation (HAXPES and XPS).

The zero-excess solid-state Na battery approach (PEEM and LEEM).

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Introduction to Li ion and Na ion batteries: why Li or Na?

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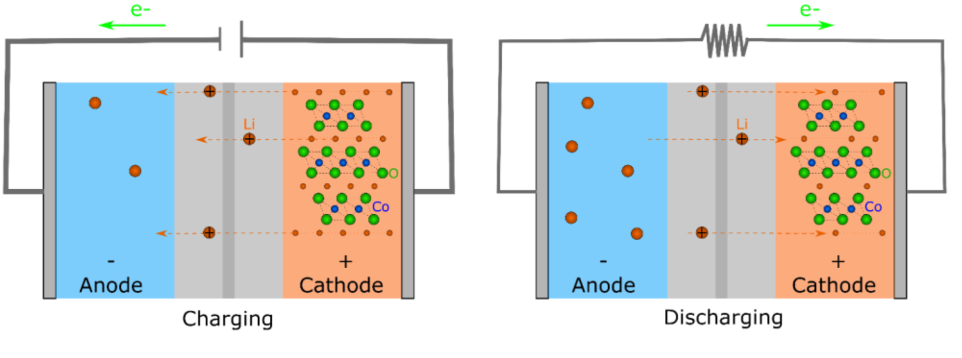
A reminder on how batteries work



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Why Li?

Lithium is a **very light and small element** (the lightest after hydrogen).

It is **highly reactive (oxidizable)** and has a very high reaction energy.

Consequently, its **mass and volume energy density is unmatched** for a solid element (hydrogen is a gas).

Its **electrochemical potential is the lowest of all elements**.

Combined with a strong oxidant, the voltage of lithium batteries is potentially unmatched.

Strongest reductant

Bad oxidant

Good oxidant

Oxydant	Réducteur	E^0 (V)
Li^+	Li	-3,04
K^+	K	-2,92
Ba^{2+}	Ba	-2,9
Ni^{2+}	Ni	-0,257
Sn^{2+}	Sn	-0,14
Pb^{2+}	Pb	-0,13
H_3O^+	$H_{2\,(g)}$	0
$O_{2\,(g)}$	H_2O	1,23
$Cr_2O_7^{2-}$	Cr^{3+}	1,33
$Cl_{2\,(aq)}$	Cl^-	1,39
PbO_2	Pb^{2+}	1,45
MnO_4^-	Mn^{2+}	1,51
Au^{3+}	Au	1,52
MnO_4^-	MnO_2	1,69
S_2	SO_4^{2-}	2,1
F_2	F^-	2,87

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Good reductant

Reduction strength

Bad reductant

Strongest oxidant

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Applications and specific energy

Portable electronics

Li-ion Battery (Mobile phone)
Tension: 3.7 V
Gravimetric energy density : 100–265 Wh/kg
Volumetric energy density : 250–700 Wh/L
Efficiency of charge/discharge: 80–90%
Self-discharge: 0.3 - 2.5 % per month
Durability (Cycling): 400–1200 cycles

Li-ion Battery (Portable computer)
Chemistry: Lithium Ions
Tension: 11.1 V
Capacity: 4400 mAh
Width: 7.5 cm

Electric vehicules

Renewable energy storage

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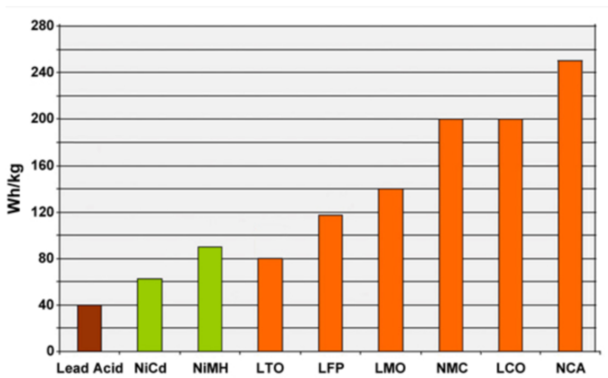
The specific energy and other problems

The specific energy of lead-, nickel- and lithium-based systems is very different. **Li-aluminum (NCA) stores more capacity** than other systems (specific energy).

In terms of **specific power and thermal stability, Li-manganese (LMO) and Li-phosphate (LFP) are superior**. **Li-titanate (LTO**) is best in terms of **life span** and also has the best cold temperature performance. **LFP** does not contain Co or Ni and **is cheaper**.



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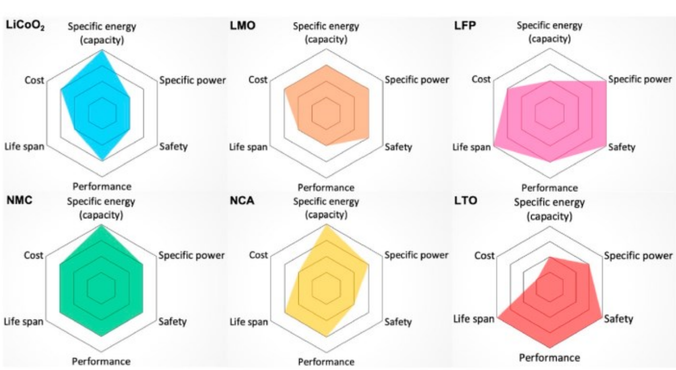
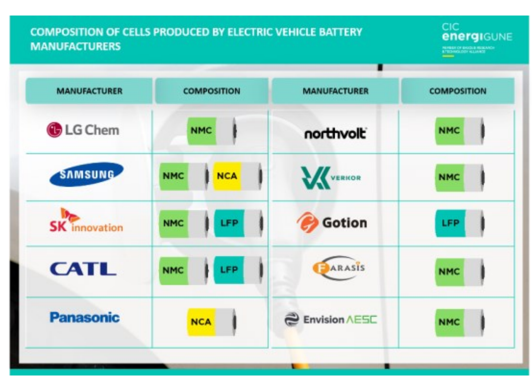
The specific energy and other problems




COMPOSITION OF CELLS PRODUCED BY ELECTRIC VEHICLE BATTERY MANUFACTURERS

CIC energiGUNE

MANUFACTURER	COMPOSITION	MANUFACTURER	COMPOSITION
LG Chem	NMC	northvolt	NMC
SAMSUNG	NMC, NCA	VERKOR	NMC
SK innovation	NMC, LFP	Gotion	LFP
CATL	NMC, LFP	FARASIS	NMC
Panasonic	NCA	Envision AESC	NMC

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Future batteries

•**Solid-state Li-ion:** High specific energy but poor loading.

•**Lithium-sulfur:** High specific energy but poor cycle life and poor loading.

•**Lithium-air:** High specific energy but poor loading, needs clean air to breath and has short life.

•**Na ion batteries:** Environmental abundance of Na, better safety and low cost, but lower energy densities and other technological problems.

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$LiCoO_2$: delithiation process and phase coexistence (ARPES, XPS and PEEM)

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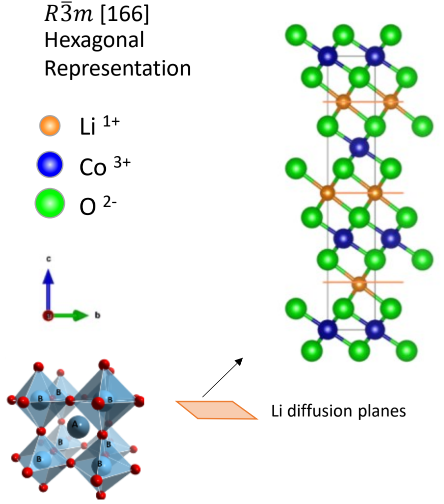
Why did Goodenough choose LiCoO2 and why was it so successful?

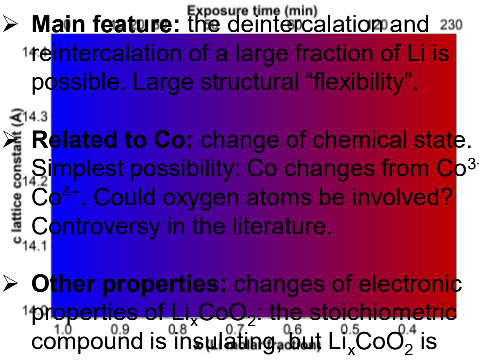
$LiCoO_2$

$R\bar{3}m$ [166]
Hexagonal
Representation



$Li_{0.5<x<1}CoO_2$

Delithiation (Li deintercalation)



- **Main feature:** the deintercalation and reintercalation of a large fraction of Li is possible. Large structural "flexibility".
- **Related to Co:** change of chemical state. Simplest possibility: Co changes from Co^{3+} to Co^{4+}. Could oxygen atoms be involved? Controversy in the literature.
- **Other properties:** changes of electronic properties of Li_xCoO_2: the stoichiometric compound is insulating, but Li_xCoO_2 is metallic.

* K.Miyoshi et al, 10.1103/PhysRevB.98.195106, PRB 98 (2018)
** E.Salagre et al, 10.1038/s41598-021-91051-3, Sci.Rep (2021)

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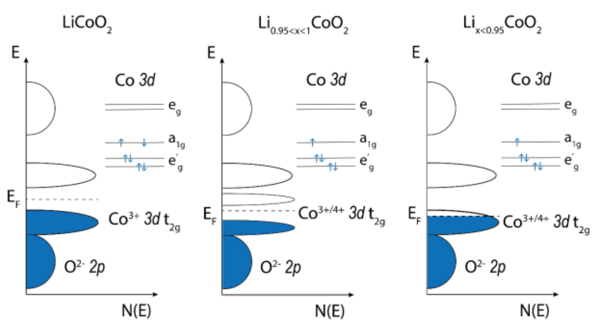
The insulator-metal transition in Li_xCoO_2

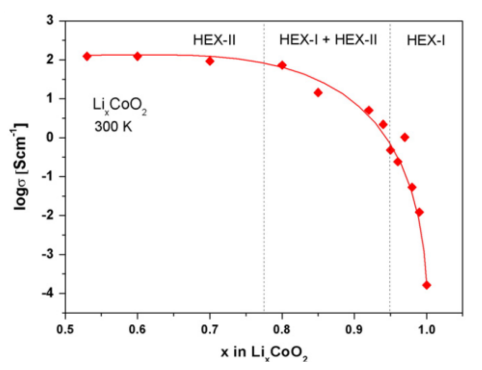
$Li_{0.5<x<1}CoO_2$

Delithiation (Li deintercalation)



Band Insulator Insulator Metal

Conductivity at 300 K vs. Li content



A. Milewska et al. Solid State Ionics 263 (2014) 110–118

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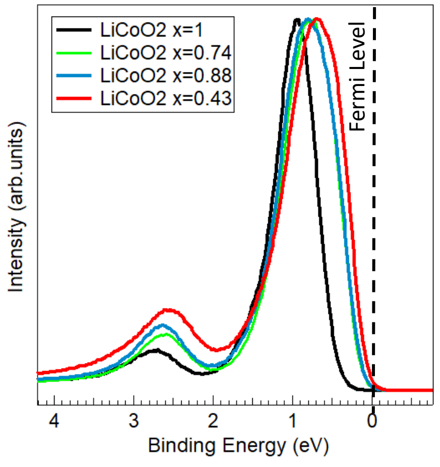
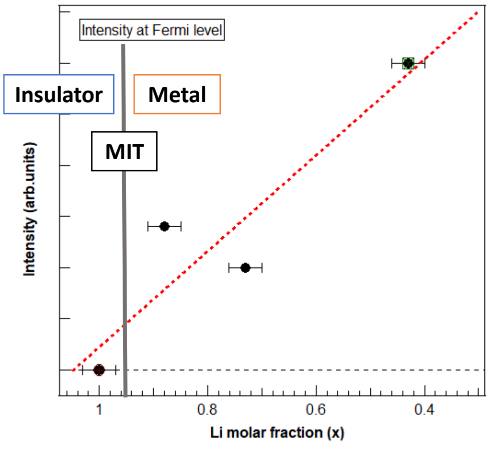
$LiCoO_2$: band structure and metallization





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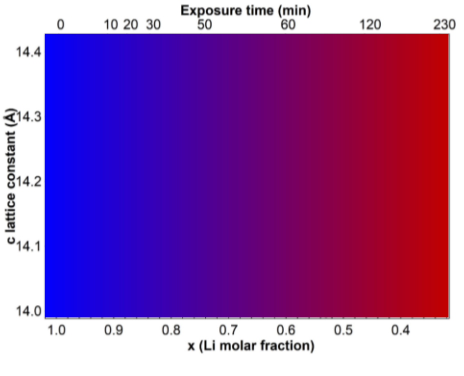
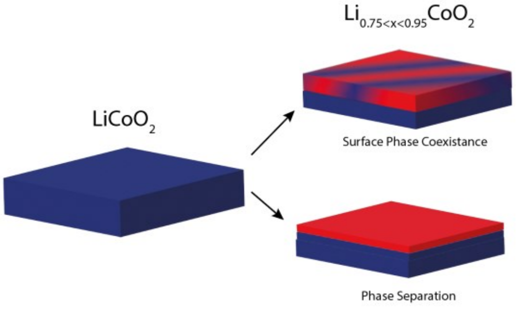
Phase Coexistence and Surface Evolution





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* K.Miyoshi et al, 10.1103/PhysRevB.98.195106, PRB 98 (2018)
** E.Salagre et al, 10.1038/s41598-021-91051-3, Sci.Rep (2021)

***Based on calculations by N. Nadkarni et al, 10.1002/ADFM.201902821, Adv. Funct. Mater. 29 (2019)

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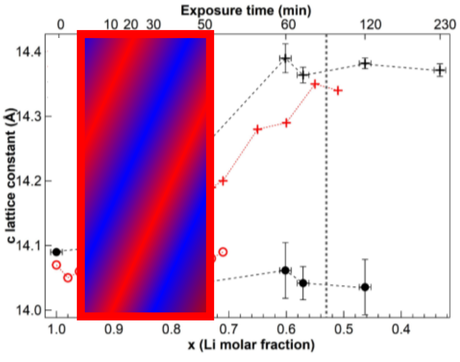
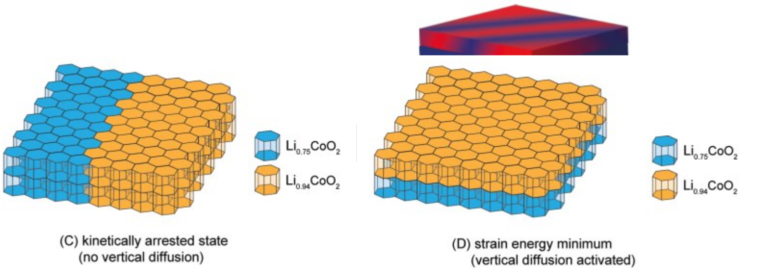
Phase Coexistence and Surface Evolution



Theoretical calculations by N. Nadkarni et al, predict phase separation for 0.75<x<0.94, with two possible scenarios depending on the amount of Li diffusion: $Li_{0.75<x<0.95}CoO_2$



Adv. Funct. Mater. 29 (2019) 1902821

* *K.Miyoshi et al, 10.1103/PhysRevB.98.195106, PRB 98 (2018)*
** *E.Salagre et al, 10.1038/s41598-021-91051-3, Sci.Rep (2021)*

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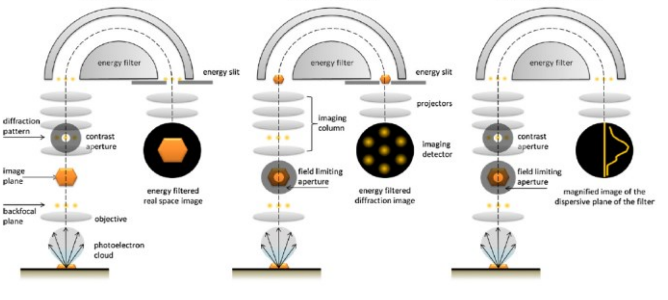
Spectromicroscopy: SPELEEM

Spectroscopic PhotoEmission and Low Energy Electron Microscope (SPELEEM) combines a Low-Energy Electron Microscope (LEEM) with an imaging energy analyzer and is key to obtaining real time characterization of both local chemical and structural information.



spatial resolution
LEEM : 10 nm
XPEEM : 25 nm

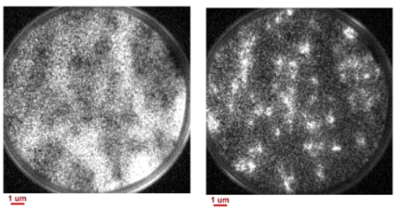
energy resolution
XPEEM : 0.3 eV

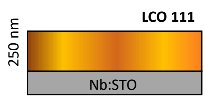
Detector blanking available for time-resolved XMCD-PEEM: see Ultramicroscopy 202, 10-17 (2019)

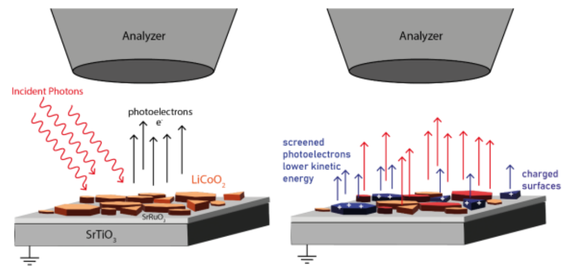
Limited: to 2 microns in dia.
Energy resolution:
ARPES: 0.3 eV
angular resolution
ARPES: 0.01 Å^{-1}

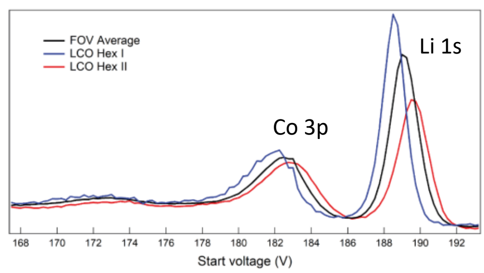
Spectromicroscopy: SPELEEM

PEEM: Li 1s XPS image









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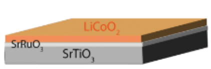
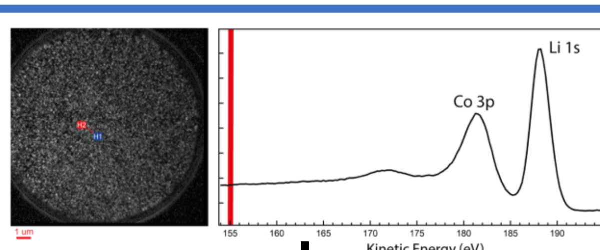
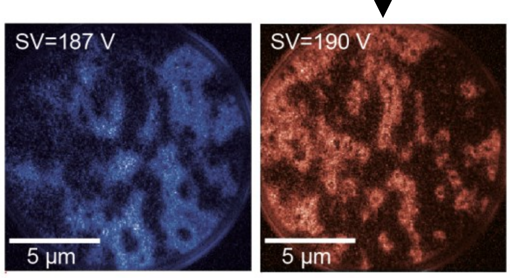
Surface spatial distribution of Li/Co concentration

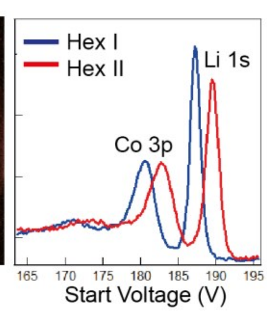




Each single region can be studied, depending on Li concentration and charge shift



PEEM



Correlations between Li/Co ratio and insulating behaviour

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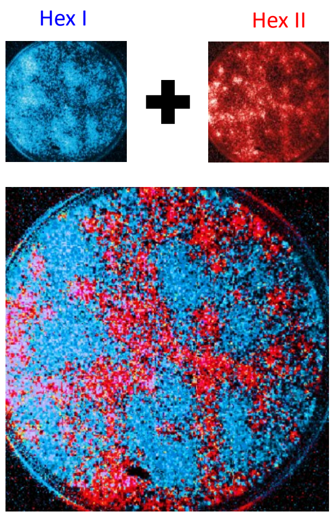
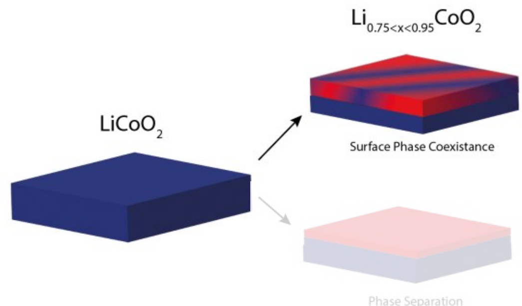
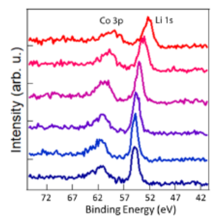
Surface spatial distribution of Li/Co concentration







Gradual Change from insulator to metal regions in the surface suggest no clear domain walls are formed at nanometer scale when no Li planes are exposed

ACS Nano 2022, 16, 16363.

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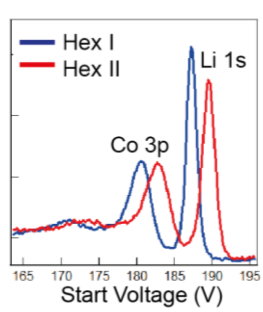
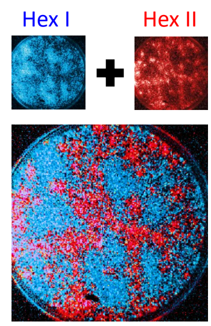
$LiCoO_2$ delithiation and phase coexistence summary

- **XPS and XAS** provide a full view of the **chemical changes** related to **cathode delithiation (charging)**
- The insulator-metal transition in $LiCoO_2$ generates phase coexistence duringthe operation range of the cathode.
- Combined **XPS and PEEM solve the real space distribution of phases, their coexistence and domain growth.**





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Solid-state batteries: mitigating mechanical failure (HAXPES and XPS)

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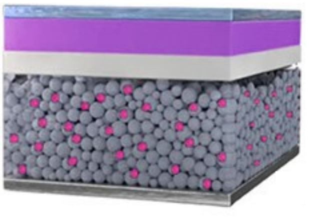
Solid-state batteries



A solid-state battery is a type of battery that uses a solid electrolyte instead of a liquid or gel electrolyte.

- Excellent theoretical energy density.
- Safer (no flammable liquid electrolytes)
- Faster charging and higher voltage

Problems:
- High cost.
- Poor operation at low temperatures.
- Mechanical failure: volume changes of cathode and anode during charge/discharge.
- Interfacial instability (side reactions take place at the electrolyte-electrode contacts).

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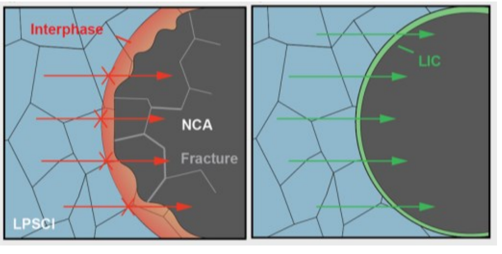
Coating strategy

Argyrodite-type solid electrolytes like Li_6PS_5Cl (LPSCl) are promising candidates, owing to its high ionic conductivity, favorable mechanical performance, and ease in processing.

However, volumetric changes in electrodes generate interfacial contact-loss during electrochemical cycling, undesirable side reactions with cathodes, and fast capacity fade.



Problem: the interphase between the electrolyte LPSCl and the cathode $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) is unstable.

Strategy: interface engineering to generate a stable interphase, using a protective layer of Li_3InCl_6.

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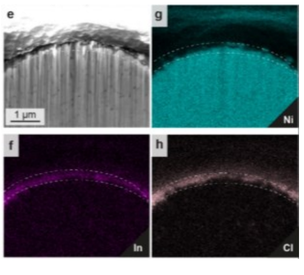
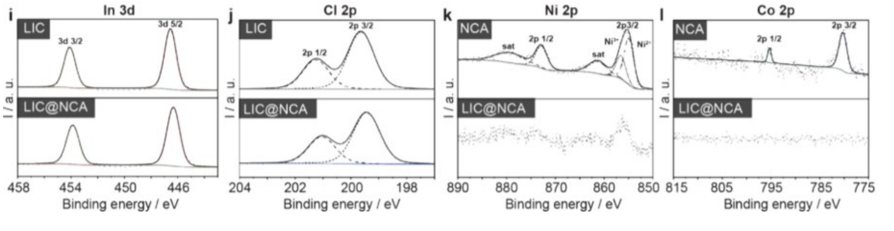
Coating effects



FIB-SEM image of LIC@NCA and EDS mapping

XPS spectra for LIC and LIC@NCA



The starting LIC covered NCA shows **good structural properties and a well-defined interphase**.

Chem. Mater. 2024, 36, 6017

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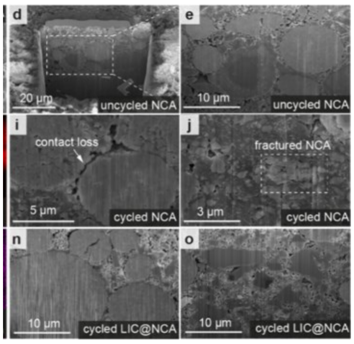
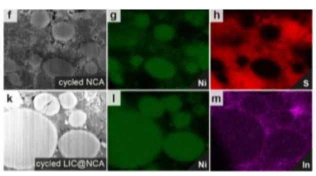
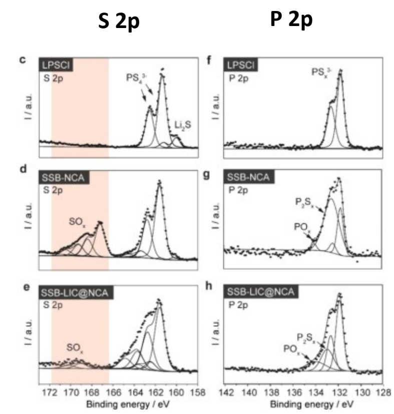
Coating effects



The LIC@NCA shows better structural properties after cycling.



FIB-SEM image of cycled NCA and LIC@NCA and EDS mapping



LIC acts as a protective layer and prevents the formation of an unstable interphase, with oxidized S compounds.

Chem. Mater. 2024, 36, 6017−6026

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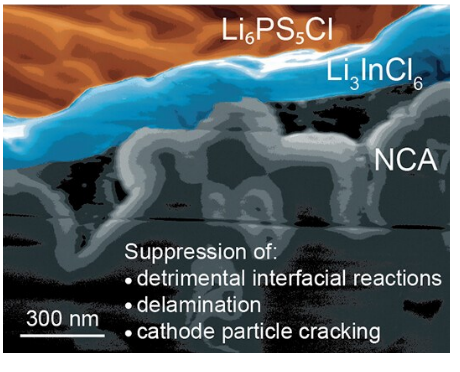
Coating effects



Chem. Mater. 2024, 36, 6017−6026

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Learning about cathodes

$LiNiMnCoO_2$ — NMC is a cathode combination of Ni-Mn-Co. NMC is the cathode of choice for power tools, e-bikes and other electric powertrains. The cathode combination is typically one-third Ni, one-third Mn and one-third Co, also known as 1-1-1. A successful combination is NCM532 with 5 parts Ni, 3 parts Co and 2 parts Mn. Other combinations are NMC622 and NMC811.

Combining the metals enhances each other's strengths:

- Co is expensive and in limited supply.
- Ni is known for its high specific energy but poor stability. Co stabilizes Ni.
- Mn has the benefit of forming a spinel structure to achieve low internal resistance but offers a low specific energy.

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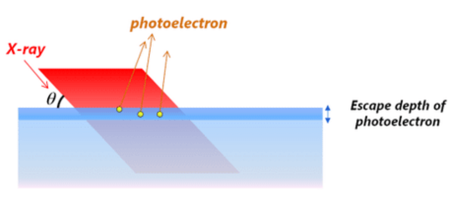
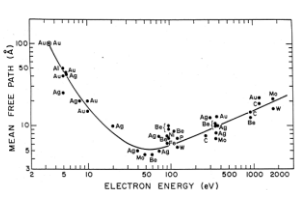
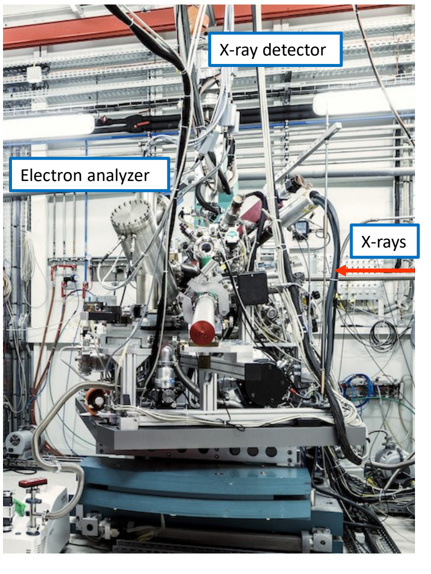
HAXPES@Spline beamline

High-energy electrons excited by x-rays (kinetic energy ~ 10 keV) and coming from deep layers and provide information about the chemical state of battery cathodes in the HAXPES (High-energy x-ray photoelectron spectroscopy) technique at Spline beamline (ESRF).





Due to the large kinetic energy, the escape depth of HAXPES photoelectrons is in the range of tens of nm, vs. 1-2 nm in conventional XPS.



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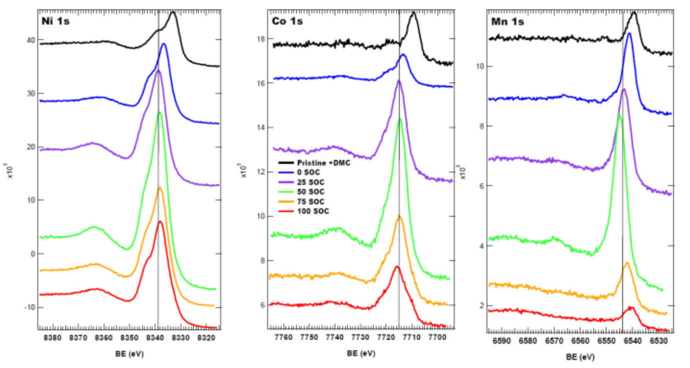
Learning about cathodes

Ni, Co and Mn 1s core levels probed by HAXPES

NMC811 cathodes are probed as a function of the state-of-charge (SOC), i.e. the Li content of the cathode material.
The delithiation process related to charging is related to a modification of the oxidation state of the metal. Each metal is modified in a different way, which can be monitored by HAXPES.



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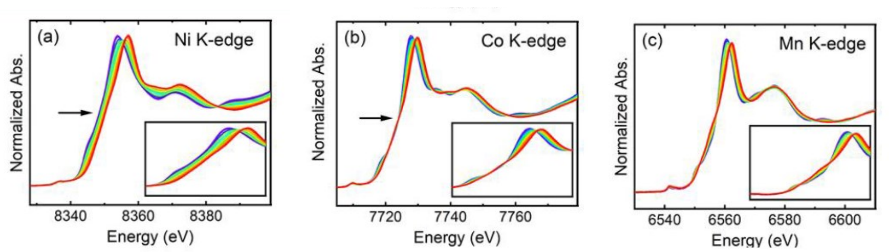
Learning about cathodes



The changes in the electronic structure related to the cathode delithiation process (battery charging) are also monitored by XAS of the K edges of Ni, Co and Mn.

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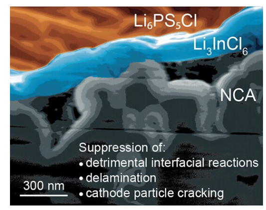
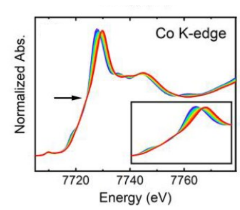
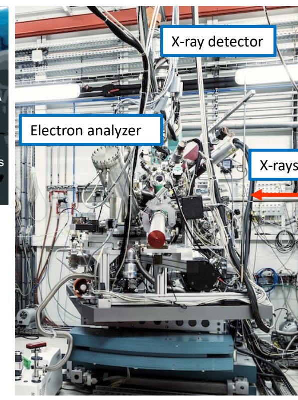
Mitigating mechanical failure summary

- **XPS and HAXPES** to understand interface chemistry
- Engineering growth techniques to **reduce interface reactions: coating**
- Combined **XPS, HAXPES and XAS** provides a complete view of the interface chemistry at different probing depths.







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The zero-excess solid-state Na battery approach (PEEM and LEEM)

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Zero excess solid state batteries (ZESSB)

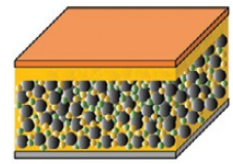
- Batteries are a key component of the energy transition
- In zero excess (zero Li/Na excess) batteries, the anode is formed in-situ during the first charging cycle, **optimizing material use**
- Solid state electrolyte with high ionic and low electronic conductivity: e.g. LaLiZrTaO or NaGdSiO

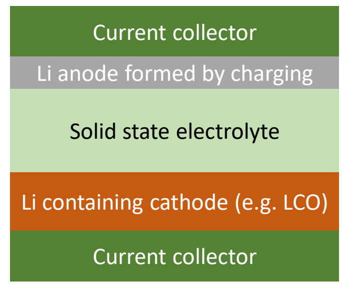
Advantages

Energy density, safety, lifespan, fast charging

Problems:

Cost, production, mechanical stability, interfacial instability





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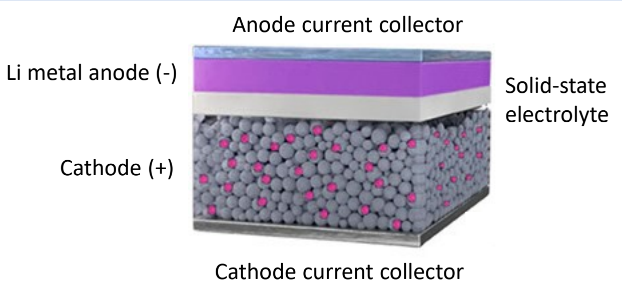
Solid-state batteries



A solid-state battery is a type of battery that uses a solid electrolyte instead of a liquid or gel electrolyte.

- Excellent theoretical energy density.
- Safer (no flammable liquid electrolytes)
- Faster charging and higher voltage

Problems:

- High cost.
- Poor operation at low temperatures.
- Mechanical failure: volume changes of cathode and anode during charge/discharge.
- Interfacial instability (side reactions take place at the electrolyte-electrode contacts).

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Learning about ZESSB with synchrotron radiation

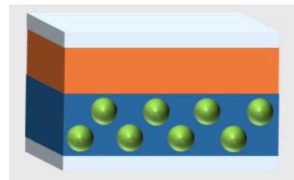
- What happens during the initial state of **anode formation** in anode-less solid-state Li and Na batteries?
- How can we **tailor the nucleation and growth of the anode**?

Nanoscale multiparameter **operando mapping** of the **battery interfaces**:

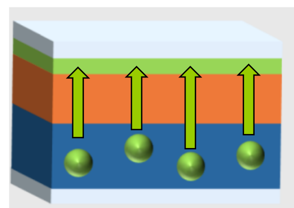
multiaxial stress fields, microstructure, phase distribution, chemical composition, oxidation state, impedance, degradation .

- Development of novel **operando synchrotron techniques** at ESRF, ALBA and DESY with nanometer resolution.
- **Multiscale modelling** assisted by a machine learning framework.

Discharged



Charged



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People

Univ. Autonoma Madrid
E. Salagre
J. Díaz-Sánchez
P. Hernández-Martín
P. Segovia
C. Polop
E.G. Michel

Univ. Complutense Madrid
M.A. González-Barrio
A. Mascaraque

Sandia National Laboratories
E.J. Fuller
A.A. Talin

CSIC
J. Rubio-Zuazo

ALBA
M. Foerster
M.A. Niño

Elettra Sincrotrone Trieste
A. Locatelli
T.O. Mentes

University of Maryland
J. Pearson
R.S. Wang
I. Takeuchi

NTNU
F. Jin
D. Rettenwander

Fraunhofer IKTS
R. Anton
A. Lowack
N. Zapp
K. Nikolowski

Ministerio de Ciencia, Innovación y Universidades
Agencia Estatal de Investigación

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