

# Electronic Structure as a Fingerprint of Thermodynamic Stability of Layered Structure Cathode Materials and of their Chemical Compatibility with Electrolytes

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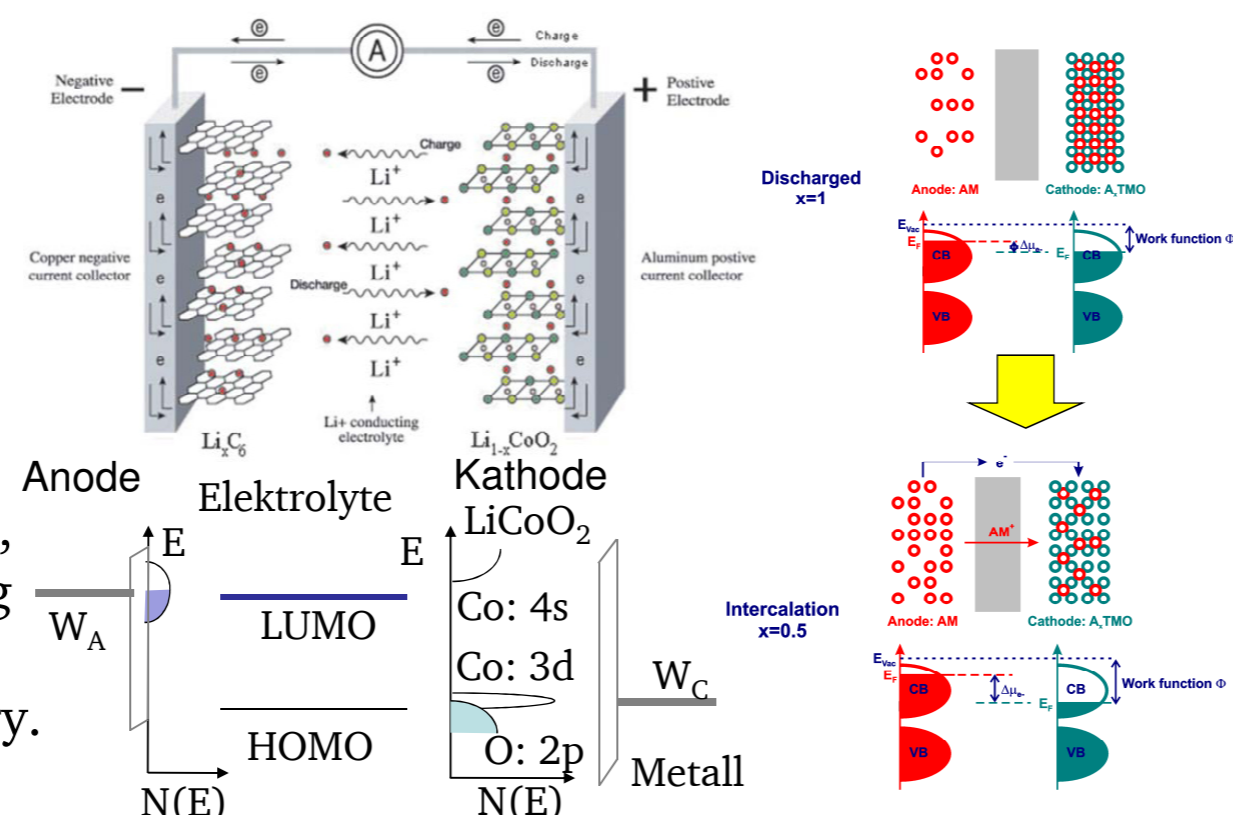
## Project A3

## Motivation

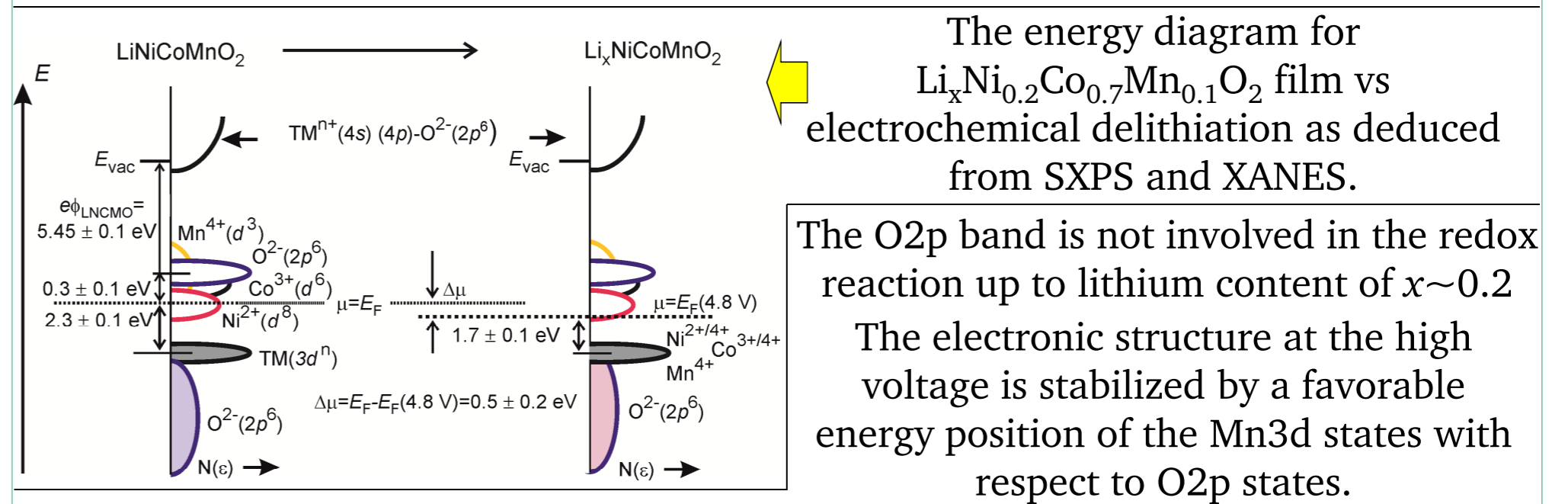
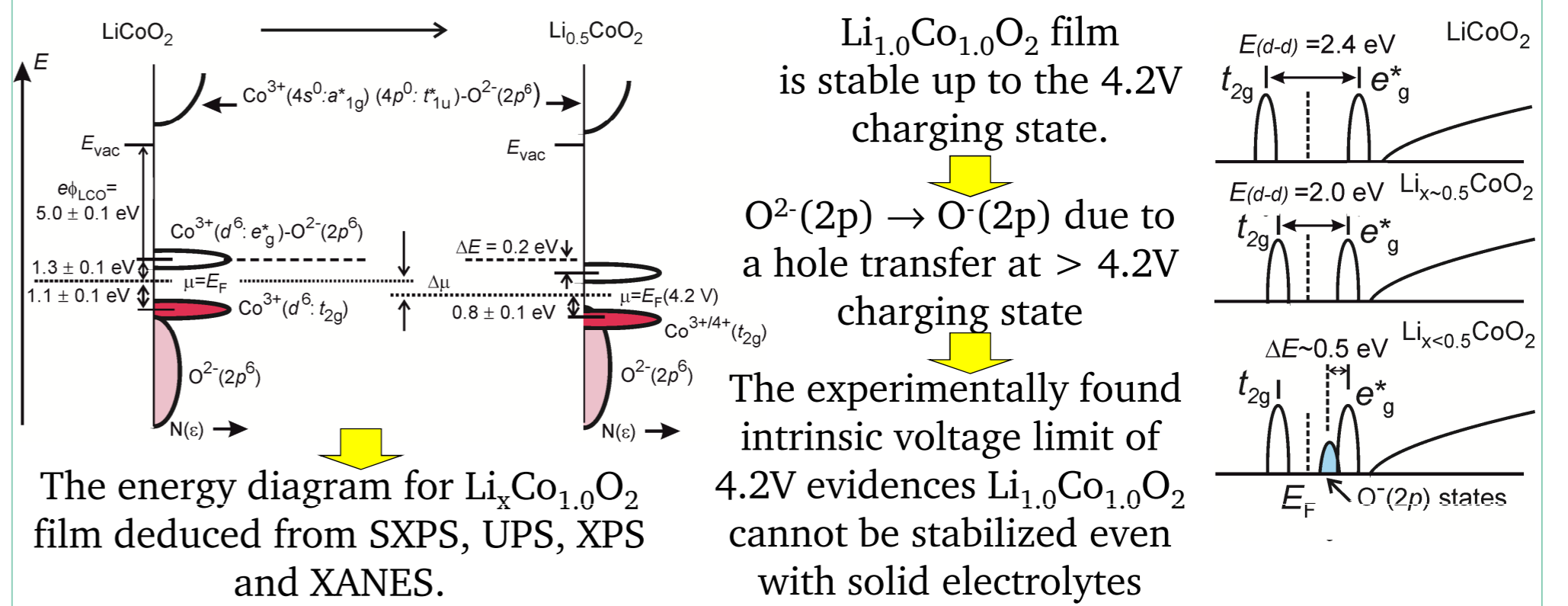
• Thermodynamic stability of any material is determined by its electronic configuration. Thus, the knowledge of the evolution of the electron structure of the electrode material impacted by external stimuli like temperature, pressure, voltage, chemical reactions at the electrode-interface, is a key factor in the understanding of thermodynamic stability of a whole Li-ion rechargeable battery.

• We focus on the *in-situ* study of the electronic structure of the cathode materials and their interfaces by using electron spectroscopy techniques like SXPS, XPS, HAPES, soft- and hard- XAS, UPS, HREELS etc. Such complex approach allows to shed light on the nature of fatigue mechanism of the model systems in order to transfer this knowledge for the explanation of the degradation mechanism occurring in the actual batteries supplied by industry.

• The *thin film* electrode material prepared under vacuum conditions can be considered as a model system for the battery application, since thin films are contamination free and the electronic and crystallographic structures are not perturbed by adsorbates from ambient. In the absence of impurities in the bulk material and on the surface and of unwanted chemical reactions with ambient, the information experimentally obtained on the electronic properties of film electrode material is unambiguous.

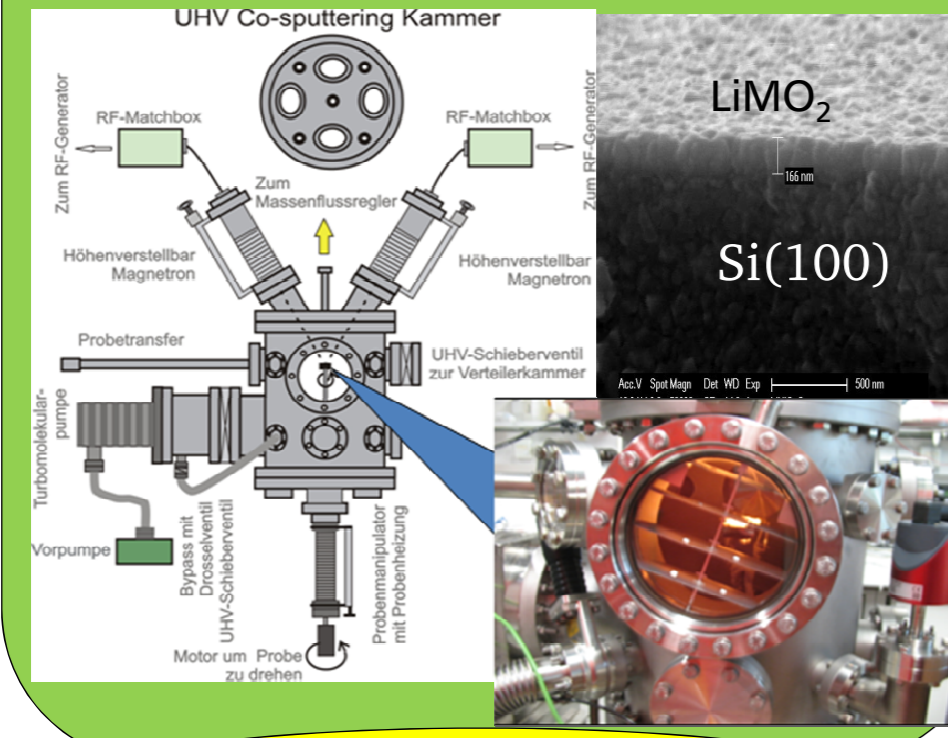


## Results

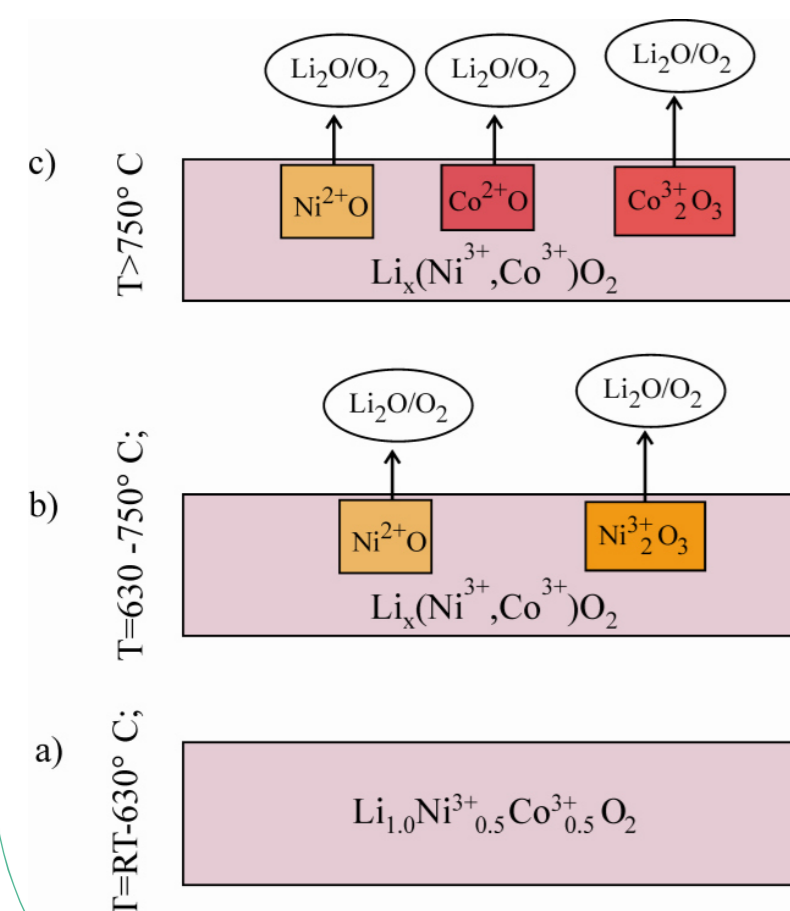
Thermodynamic stability of the LiMO<sub>2</sub> Film Battery Cells under Electrochemical Li-Deintercalation/Intercalation

## Results

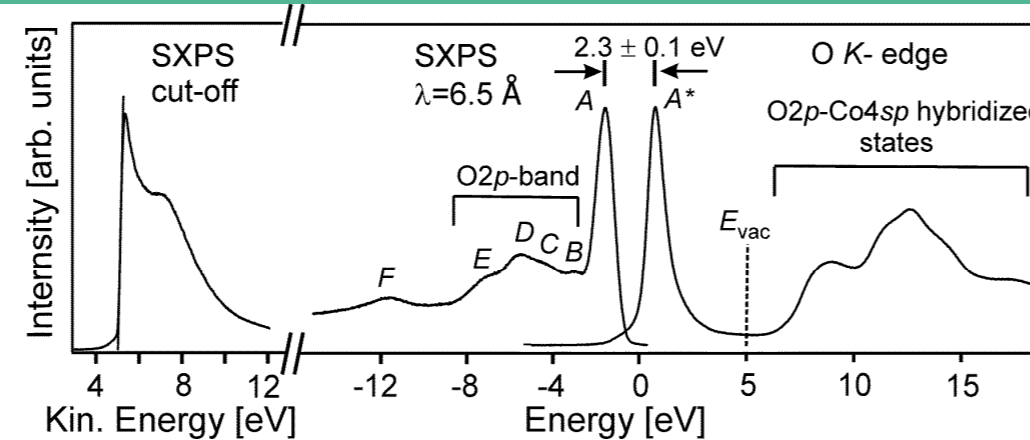
## RF co-sputtering chamber for growing complex thin film cathode materials.



Up to 4 target materials can be simultaneously deposited



Li(Ni, Co, Mn)O<sub>2</sub>: Ni<sup>2+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>3</sup>↓e<sub>g</sub><sup>2</sup>↑) LS, Co<sup>3+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>3</sup>↓e<sub>g</sub><sup>0</sup>) LS and Mn<sup>4+</sup>(t<sub>2g</sub><sup>3</sup>↑e<sub>g</sub><sup>0</sup>) electronic configurations are formed at 500°C < T<sub>ann</sub> < 700°C at 1E-2 ≤ p<sub>O2</sub> ≤ 10 mbar. T<sub>ann</sub> > 700°C → the reduction of the Co<sup>3+</sup> and Mn<sup>4+</sup> ions.



The density of occupied and unoccupied electron states of Li<sub>1.0</sub>Co<sub>1.0</sub>O<sub>2</sub> film probed by SXPS, UPS, XPS and XANES.

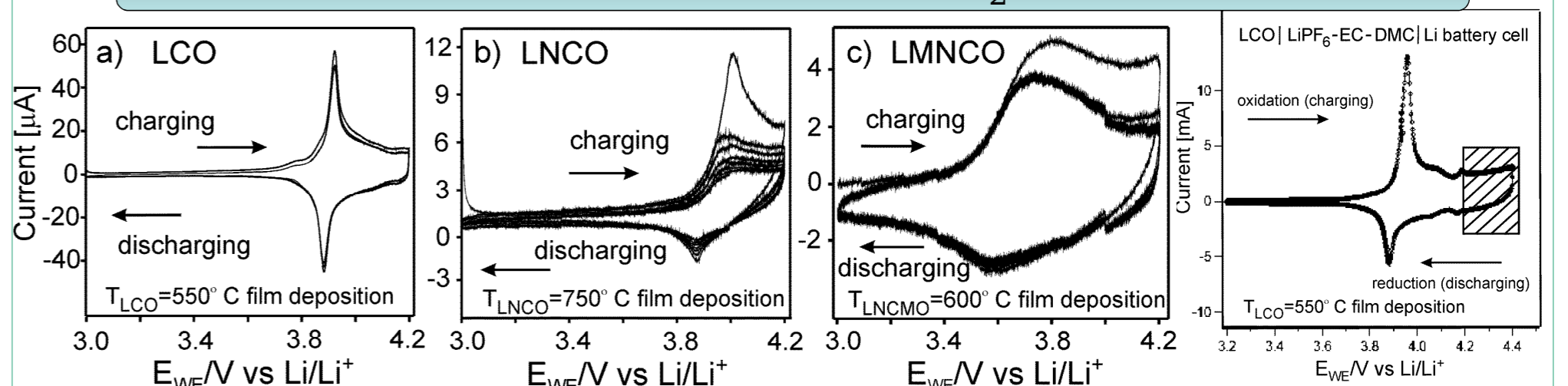
Thermodynamic stability of the R3-m layered LiMO<sub>2</sub> film cathode materials under preparation conditions

LiCoO<sub>2</sub> stoichiometric film material with well-crystallized structure and of Co<sup>3+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>3</sup>↓e<sub>g</sub><sup>0</sup>) with low spin (LS) electronic configuration is formed at 400-650°C. It is not stable at higher temperatures → the formation of Co<sup>2+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>2</sup>↓e<sub>g</sub><sup>2</sup>↑) ions with HS state and oxygen vacancies.

Li(Ni,Co)O<sub>2</sub>: Co<sup>3+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>3</sup>↓e<sub>g</sub><sup>0</sup>) with LS and Ni<sup>3+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>3</sup>↓e<sub>g</sub><sup>1</sup>) with LS electronic configurations are formed at the similar temperature and pressure ranges that for LCO. High temperatures are needed for crystallization. Unstable at T<sub>ann</sub> > 630°C → the lithium and oxygen loss; occupation of the lithium vacancies by Ni<sup>2+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>3</sup>↓e<sub>g</sub><sup>2</sup>↑) ions. T<sub>ann</sub> > 750°C → phase separation.

Chemical Compatibility of the LiMO<sub>2</sub> cathode materials with electrolytes

- LiCoO<sub>2</sub>/LiClO<sub>4</sub>-PC interface: formation of SEI layer (Li<sub>x</sub>O<sub>y</sub>, Li<sub>2</sub>CO<sub>3</sub>);
- Li(Ni,Co)O<sub>2</sub>/LiClO<sub>4</sub>-PC: formation of (a) SEI layer (Li<sub>x</sub>O<sub>y</sub>, LiCO<sub>3</sub>), (b) the oxygen vacancies, (c) Co<sup>3+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>3</sup>↓e<sub>g</sub><sup>0</sup>) → Co<sup>2+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>2</sup>↓e<sub>g</sub><sup>2</sup>↑) ions reduction.
- Li(Ni,Co,Mn)O<sub>2</sub>/LiPF<sub>6</sub>-EC-DMC/PVDF/C: formation of (a) LiF, LiP<sub>x</sub>F<sub>y</sub>, Li<sub>x</sub>O<sub>y</sub>, Li<sub>2</sub>CO<sub>3</sub> (b) oxygen vacancies.
- Li(Ni,Co,Mn)O<sub>2</sub>/LiPF<sub>6</sub>-EC-DMC-2%VC interface: suppression of the involving Ni<sup>2+</sup> ions at the interface in the charge compensation caused by Li-deintercalation.

Electrochemical Performance of the LiMO<sub>2</sub> thin film batter cells.

CV characteristics of the LiMO<sub>2</sub> film battery cells. A Li-foil as the anode, PC-LiClO<sub>4</sub>- and EC-DMC-LiPF<sub>6</sub>- electrolytes were used. The marked area denotes the instability region of Li<sub>x</sub>CoO<sub>2</sub>. The capacity drop observed in the Ni-containing electrodes is due to occupation of the Li- vacancies by Ni<sup>2+</sup>(t<sub>2g</sub><sup>3</sup>↑t<sub>2g</sub><sup>3</sup>↓e<sub>g</sub><sup>2</sup>↑) with HS ions during the electrochemical cycling.

## Conclusion

- LiCoO<sub>2</sub> is thermodynamic stable under the preparation conditions. Thermodynamic stability under electrochemical delithiation is limited by the intrinsic voltage limit of 4.2V, this material cannot be used for the high voltage application even with chemically compatible solid state electrolytes.
- Li(Ni,Co)O<sub>2</sub> is thermodynamic stable under the charging state of < 4.4 V. Increase of the voltage window is due to the favorable energy position of Ni3d(e<sub>g</sub>) band.
- Li(Ni,Co,Mn)O<sub>2</sub> is thermodynamic stable under the charging state of ≤ 4.6 V.
- The Ni-containing electrodes are difficult in the growing stoichiometric films. The Ni<sup>3+</sup> ions tend to be reduced to Ni<sup>2+</sup> state during both the film preparation and the cycling. The Ni<sup>2+</sup> ions is the reason of the cation mixing.
- The electrode-electrolyte interface impacts strongly on the electronic structure of the transition metal oxides; can blocks the Li<sup>+</sup> transport through the interface due to the electrode-electrolyte chemical reactions.

## 5 Key Publications (2003-2014)

1. D. Ensling, G. Cherkashin, S. Schmid *et al*, CHEM. MATER., **26** (2014) 3948.
2. G. Cherkashin, D. Ensling, W. Jaegermann, J. MATER. CHEM. A, **2** (2014) 3571.
3. D. Ensling, A. Thissen, S. Laubach *et al*, Electronic structure of LiCo<sub>2</sub> thin films: A combined photoemission spectroscopy and density functional theory study, PHYS. REV. B, **82** (2010) 195431.
4. D. Ensling, A. Thissen, W. Jaegermann, On the formation of lithium oxides and carbonates on Li metal electrodes in comparison to LiCo<sub>2</sub> surface phases investigated by photoelectron spectroscopy, APPL. SURF. SCI. **255** (2008) 2517.
5. Q.-H. Wu, A. Thißen, W. Jaegermann *et al*, Resonant photoemission spectroscopy study of electronic structure of V<sub>2</sub>O<sub>5</sub>, CHEM. PHYS. LET. **430** (2006) 309.

## Publications last funding period

- 1) D. Ensling, G. Cherkashin, S. Schmid *et al*, Non-rigid band behavior of the electronic structure of LiCo<sub>2</sub> thin film during electrochemical Li-deintercalation. CHEM. MATER., **26** (2014) 3948.
- 2) G. Cherkashin, D. Ensling, W. Jaegermann, LiMO<sub>2</sub> (M = Ni, Co) thin film cathode materials: a correlation between the valence state of transition metals and the electrochemical properties, J. MATER. CHEM. A, **2** (2014) 3571.
- 3) G. Cherkashin, K. Nikolowski, H. Ehrenberg *et al*, The stability of the SEI layer, surface composition and the oxidation state of transition metals at the electrolyte-cathode interface impacted by the electrochemical cycling: X-ray photoelectron spectroscopy investigation. PHYS. CHEM. CHEM. PHYS., **14** (2012) 12321.
- 4) See a complete list of the publications on a separate page.