

# Computational Design and Experimental Verification of Zero- and Low-strain Cathode Materials for Solid-State Li-ion batteries



ALWAYS A BETTER WAY

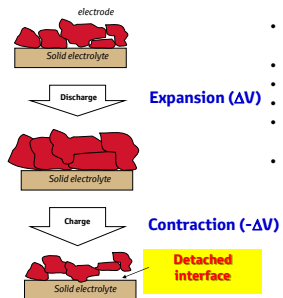


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## Background

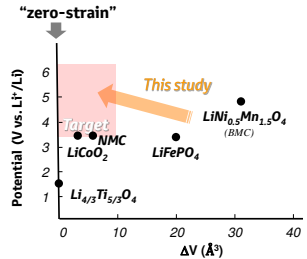
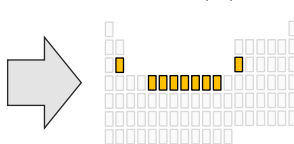
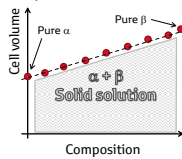


- One of the major degradation factors in Li-ion batteries is the volume change occurring upon charge and discharge in electrode materials [1].
- This volume change can be easily accommodated in conventional composite electrodes, but in the case of a rigid, solid-state battery the stress generated at the grain interfaces will lead to the destruction of the device.
- For the anode,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is a strong candidate for solid-state Li-ion batteries, giving its zero-strain properties [2].
- For the cathode, on the other hand, no viable zero-strain candidate has been described in the literature yet.
- Finding a zero-strain cathode material with high-voltage by trial-and-error is clearly not a viable strategy → ab-initio Material Design
- We employed DFT calculations to link the volume change, the composition and the lithium content of various precursor materials with the spinel structure.
- Using Vegard's law [3] we mixed the precursors to obtain materials with the desired strain properties

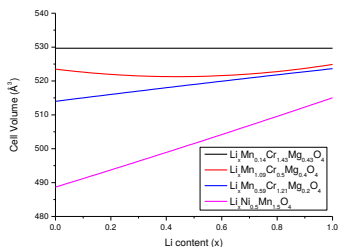
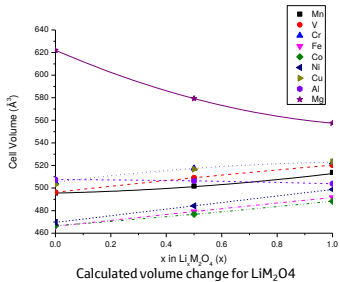
$$\alpha \rightarrow V\alpha$$

$$\beta \rightarrow V\beta$$

$$V(x\alpha + y\beta) = xV\alpha + yV\beta$$

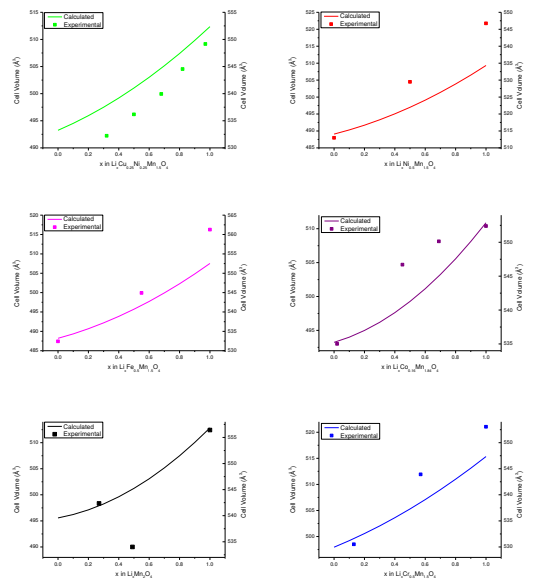


## Theoretical approach and material design

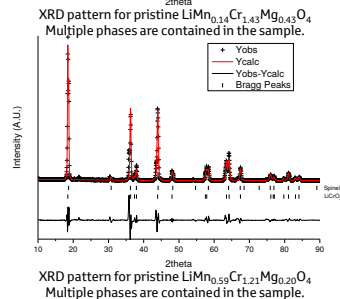
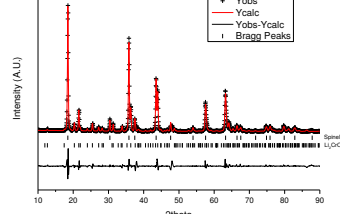


Calculated volume change for the optimized compositions

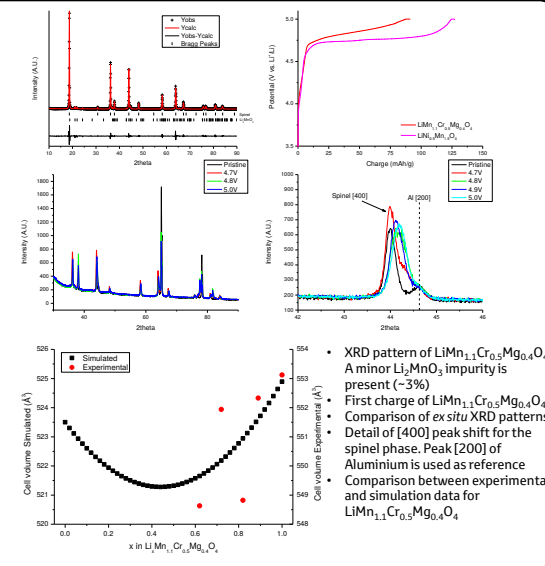
- DFT calculations of various  $\text{LiM}_2\text{O}_4$  materials in three lithiation states ( $x=0, 0.5, 1$ ) were performed and interpolated with 2<sup>nd</sup> degree polynomials.
- The behaviour of most transition metals is similar, however the behaviour of Mg is peculiar, as it is the only metal to allow for volume compensation.
- In order to maximize the available charge, 3 metals were chosen to design a zero-strain cathode material:
  - Mg in order to reduce the volume change
  - Mn to provide structural stability
  - Cr to compensate for the electrochemical inactivity of Mg
- The three base components were mixed according to three principles:
  - One free optimization to obtain a true zero-strain material
  - One optimization constraining Mn  $\geq 1$
  - One optimization constraining Mg  $\leq 0.2$
- It was possible to satisfy all three designs with the following compositions:
  - $\text{LiMn}_{0.14}\text{Cr}_{1.43}\text{Mg}_{0.43}\text{O}_4$  with projected  $\Delta V=0\text{Å}^3$
  - $\text{LiMn}_{1.1}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$  with projected  $\Delta V=3\text{Å}^3$
  - $\text{LiMn}_{0.59}\text{Cr}_{1.21}\text{Mg}_{0.2}\text{O}_4$  with projected  $\Delta V=8\text{Å}^3$
- These values compare favourably with the benchmark material  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , which has been shown to have  $\Delta V=30\text{Å}^3$  [5].
- Assuming that Manganese is in its  $\text{Mn}^{4+}$  state, by exploiting the broad Chromium redox range  $\text{Cr}^{3+/4+/6+}$  it should be possible to extract all Lithium from these materials.
- Additionally, in order to validate the method, the simulation results were compared with data obtained from the literature: the general trend of the volume change is reflected in the simulation, with the typical shift due to the DFT method.



## Experimental verification



- Powders of the three materials were prepared by solid state synthesis, using  $\text{Li}_2\text{CO}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}_2$ , and  $\text{MgO}$  as precursors. The reagents were mixed in an agate mortar, pelleted, and heated to 900°C for 24h in air.
- Electrochemical cells were built in Swagelok configuration with Li as negative and pseudo-reference electrode, and LP30 as electrolyte.
- The XRD pattern of  $\text{LiMn}_{0.14}\text{Cr}_{1.43}\text{Mg}_{0.43}\text{O}_4$  shows clearly the presence of two phases. This is consistent with the fact that  $\text{LiCr}_2\text{O}_4$  does not exist, thus making it difficult to prepare high-Cr containing spinels.
- Similarly, the XRD pattern of  $\text{LiMn}_{0.59}\text{Cr}_{1.21}\text{Mg}_{0.2}\text{O}_4$  shows the presence of at least three phases. High-Cr spinels do not seem to be synthesizable.
- On the other hand,  $\text{LiMn}_{1.1}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$  could be synthesized in mostly pure form, with a minor impurity of  $\text{Li}_2\text{MnO}_3$ .
- $\text{LiMn}_{1.1}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$  was used to build electrochemical cells in order to study the volume change upon delithiation. *Ex situ* XRD patterns were taken of electrodes charged at 4.7V, 4.8V, 4.9V and 5.0V vs. Li<sup>+</sup>/Li. The Aluminium foil provided the internal reference for alignment of the patterns
- From the experimental results it is possible to observe that:
  - The charge extracted from the material up to 5.0V vs. Li<sup>+</sup>/Li is not consistent with the expected theoretical capacity of 160 mAh/g: the full oxidation of chromium up to  $\text{Cr}^{6+}$  is only possible above this potential
  - The material reacts to delithiation by expanding and contracting in a narrow range of circa 4Å<sup>3</sup>, well consistent with the calculated strain



## Conclusions

- We have used DFT to design high-voltage, low-strain cathode materials for Li-ion batteries
- We could confirm good agreement between calculated and experimental data
- $\text{LiMn}_{1.1}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$  could be used as low-strain cathode material in solid-state Li-ion batteries

## References

- [1] Science, 342, 716
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