

Low-Strain Cathode Materials for Solid-State Li-Ion Batteries

The volume change of active materials that accompanies charge and discharge of Li-ion batteries is a major source of degradation, which limits the overall lifetime of such a battery [1]. While a zero-strain anode material exists, namely $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [2], no suitable zero- or low-strain cathode material is known so far. By using systematic DFT calculations, three low-strain materials have been identified within the class of $\text{LiMn}_{2-y-z}\text{Cr}_y\text{Mg}_z\text{O}_4$. The most promising materials have been synthesized and characterized by X-ray diffraction and electrochemical techniques. The results are consistent with the *ab initio* predictions [3], [4].

Keywords: *Li-ion batteries, cathode materials, low-strain cathodes, transition-metal oxides*

1 Background

Long-term stability and safety are indispensable requirements in the search for new battery materials with higher capacities. While the need for safer batteries has initiated the development of solid-state electrolytes, new challenges emerged regarding the mechanical stability at the interfaces with the electrodes. Since most of the known active materials used as negative and positive electrodes experience expansion and contraction during operation, cracks will form at the interfaces with the rigid electrolyte causing degradation of the battery performance [1]. Whereas on the an-

ode side $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been shown to operate with nearly zero strain [2], a cathode material with similar properties was still missing at the time the present study was initiated. Candidate electrode materials as given in Figure 1 showed either rather low voltage or large volume change as in the case of the previous benchmark material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [5]. The present application note describes a set of *ab initio* calculations as based on density functional theory (DFT), which were performed to investigate a class of transition-metal oxides based on the spinel structure [3], [4].

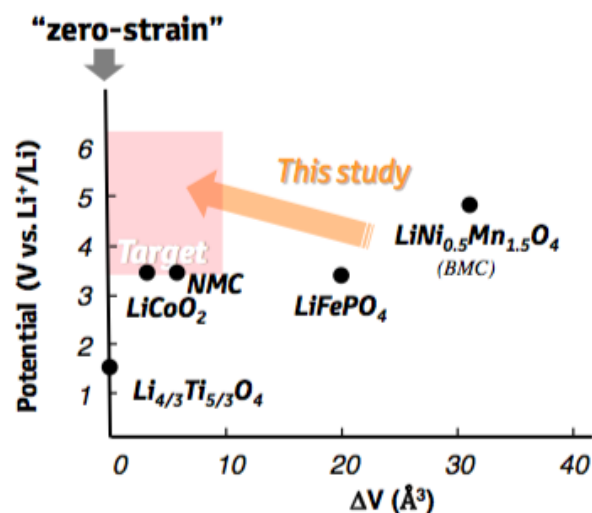


Figure 1: Li chemical potentials and volume changes of candidate cathode materials. The shaded area marks the target materials with a much lower volume change than the previous benchmark material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

2 Method of Calculation

The DFT calculations were performed using Medea® [6] VASP [7], which uses projector-

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augmented (PAW) potentials and wave functions [8]. Exchange and correlation effects were included within the semilocal GGA as parametrized by the PBEsol scheme [9]. In a first step, DFT calculations were used to evaluate the volume change of the spinel-type compounds $\text{Li}_x\text{M}_2\text{O}_4$, where $\text{M} = \text{Mg}, \text{Al}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$, on lithiation and delithiation. To this end, three different values for the lithium content were considered, namely, $x = 0, 0.5, 1.0$. All structures were fully relaxed and different spin-structures were taken into account. In addition, deviations from the cubic symmetry underlying the spinel-structure were allowed for. In a second step, the previous results were used to minimize the volume change of the quasi-ternary compounds $\text{LiM}^{1-2-y-z}\text{M}^2\text{yM}^3\text{zO}_4$ in an approach closely following Vegard's law [10].

3 Computed Results

The results of the *ab initio* calculations for the pure spinel-type compounds are summarized in Figure 2, which shows for each compound the calculated volume at the three Li concentrations mentioned above. Note that at this stage the fact that some of these compounds may not even exist in nature was ignored. The lines included in Figure 2 were obtained from parabolic fits to the data points. Obviously, all transition metals induce a volume increase with increasing lithium concentration, whereas only Al and Mg cause a decrease of the cell volume, which in case of Mg is particularly strong. As a consequence, any quasi-ternary spinel-type compound must contain a non-negligible fraction of Mg to counterbalance the vol-

ume increase of the transition-metal spinels on lithiation. Hence, Mg was the first choice to be inserted into the basic cathode material LiMn_2O_4 . Yet, since Mg is electrochemically inactive, Cr was chosen as a third partner because of the many oxidation states offered by this element.

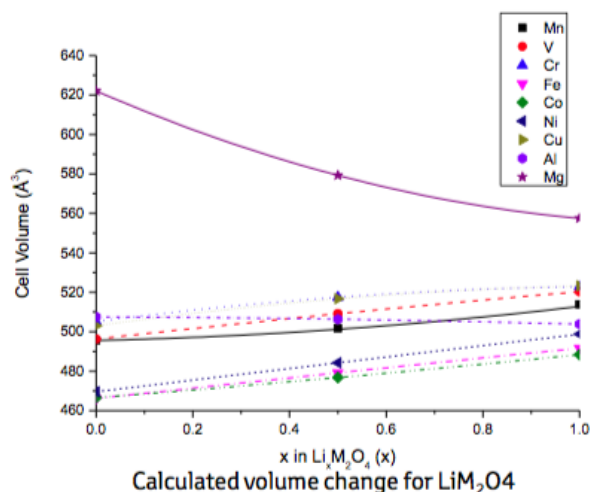


Figure 2: Calculated volume change for base spinel constituents LiM_2O_4 ($\text{M} = \text{Mg}, \text{Al}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$).

After these preparations the next step consisted of optimizing the relative concentrations at the metal sites of the quasi-ternary compound $\text{LiMn}_{2-y-z}\text{Cr}_y\text{Mg}_z\text{O}_4$ in order to minimize the volume change on lithiation and delithiation. To this end, three different approaches were used, namely, (1) full unconstrained optimization to obtain zero-strain behavior, (2) constrained optimization to find a low-strain material with Mn content $2-y-z$ larger than 1 in order to ensure structural stability, and (3) constrained optimization to find a low-strain material with Mg content z smaller than 0.2 in order to reduce the amount of highly oxidized Cr necessary to achieve full charge. The results of these three approaches together with the volume change of the benchmark compounds $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are displayed in Figure 3. As expected, unconstrained optimization indeed leads to zero volume change, however, at a very small Mn and big Cr content. More interesting are the two low-strain configurations $\text{LiMn}_{1.1}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$, and $\text{LiMn}_{0.59}\text{Cr}_{1.21}\text{Mg}_{0.2}\text{O}_4$ with volume changes of 0.6% (3 \AA^3) and 1.6% (8 \AA^3), respectively, much lower than the value of 6% (30 \AA^3) reported for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

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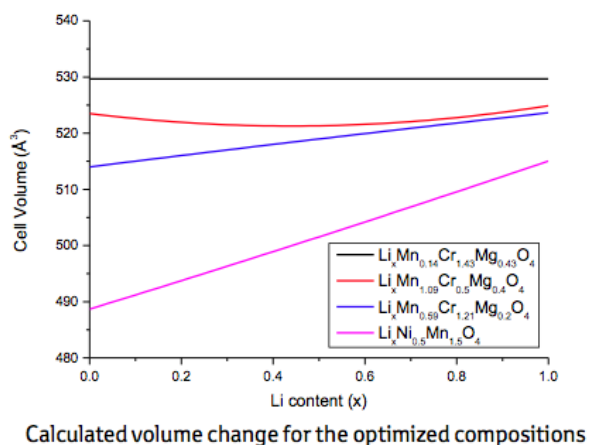


Figure 3: Calculated volume change for the optimized spinel compositions $\text{LiMn}_{0.14}\text{Cr}_{1.43}\text{Mg}_{0.43}\text{O}_4$, $\text{LiMn}_{1.1}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$, and $\text{LiMn}_{0.59}\text{Cr}_{1.21}\text{Mg}_{0.2}\text{O}_4$. The volume change for the benchmark $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is also shown.

In order to confirm the validity of the approach and to make a close connection to existing experimental data, the previous optimizations were complemented with calculations of the volume changes of a set of selected compositions, namely, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiCu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.5}\text{O}_4$, $\text{LiCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiCo}_{0.16}\text{Mn}_{1.84}\text{O}_4$, and $\text{LiAl}_{0.15}\text{Mn}_{1.85}\text{O}_4$, which were found in very good agreement with measured values in all cases [4].

Powder samples of all three optimized compounds were synthesized at Toyota Motors Europe [3]. However, XRD patterns of the two samples with high Cr concentration revealed the presence of at least two phases, indicating a phase separation induced by the high Cr content. The instability caused by high Cr content is consistent with the fact that LiCr_2O_4 does not exist. In contrast, $\text{LiMn}_{1.1}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$ could be synthesized in almost pure form and was thus used to build electrochemical cells in order to investigate the volume change upon charging and discharging the cells. As a result, *ex situ* XRD patterns showed a volume change of 4 Å in very good agreement with the calculations. In addition, charge curves taken for this system revealed a performance comparable to that of the benchmark material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

The DFT calculations also provided detailed insight into the mechanisms resulting in a near

zero-strain behavior. A synergistic compensation mechanism underlies the desired property as illustrated in Figure 4, which includes the bond lengths calculated for an eightfold supercell of $\text{Li}_x\text{Mn}_{1.125}\text{Cr}_{0.5}\text{Mg}_{0.375}\text{O}_4$. With increasing Li concentration, the Mg-O bonds tend to decrease, the Mn-O bonds remain similar, while the Cr-O bonds tend to increase. As a result, the overall volume of the crystal structure changes little upon charging and discharging with Li ions. Furthermore, the microscopic analysis thus well reflects the behavior of the “pure” compounds as displayed in Figure 1. This behavior is also in close analogy to observation for the zero-strain mechanism for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, where local distortions in the crystal structure likewise allow this material to keep the volume nearly unchanged upon lithium insertion [11].

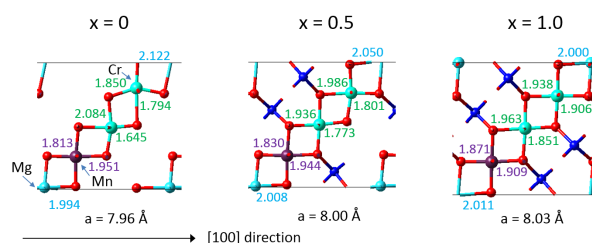


Figure 4: Calculated interatomic distances of $\text{Li}_x\text{Mn}_{1.125}\text{Cr}_{0.5}\text{Mg}_{0.375}\text{O}_4$ for increasing Li concentration.

4 Conclusion

In this project, DFT simulations have been combined with an optimization approach based on Vegard’s law to obtain a spinel-type quasi-ternary compound with small volume change on lithiation and delithiation. The procedure has been confirmed by comparison to measured volume changes obtained for various compositions. In addition, experiments performed for the best candidate, $\text{LiMn}_{1.1}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$, found a volume change of 0.8% (4 Å³) in very good agreement with the calculated 0.6% (3 Å³). Finally, analysis of the DFT results allowed to understand the observed volume changes from a microscopic compensation mechanism.

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MedeA modules used in this application

- MedeA Environment
- MedeA VASP