Zr Incorporation into Lithium Nickel Oxides: Solid Solution or Two-Phase System

Lars Winkler, and Payam Kaghazchi*

Institute of Energy Materials and Devices (IMD) – IMD-2: Materials Synthesis and Processing, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

MESA+ Institute for Nanotechnology, University of Twente, P. O. Box 217, Enschede 7500AE, The Netherlands

l.winkler@fz-juelich.de

**p.kaghazchi@fz-juelich.de*

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Ni-rich cathodes such as $LiNiO_2$ (LNO) offer high theoretical capacities for Li-ion batteries, but their performance degrades upon cycling due to limiting factors such as microcracking, electrolyte decomposition, cation mixing and/or oxygen loss. A common strategy to mitigate these degradation mechanisms involves the use of doping and/or coating agents to enhance structural stability and capacity retention. Cobalt, alumina, and manganese – used in NCA and NCM cathodes – are well-known examples that improve cycling performance, although they reduce the overall theoretical capacity compared to pure LNO. Therefore, ongoing research aims to identify alternative doping and coating agents that can stabilize LNO while preserving its high theoretical capacity. Zirconium is a promising candidate, with studies reporting improved capacity retention when LNO is doped with small amounts of Zr. However, incorporating Zr into the LNO lattice remains challenging, even with low doping concentrations.

This study focuses on the incorporation of Zr into LNO using electrostatic analysis and *ab-initio* density functional theory (DFT) calculation. We analysed the synthesis route using common precursor materials, which can yield either a mixture of pure LNO and Li_2ZrO_3 (LZO), or Zr-doped LNO ($Li_xNi_yZr_ZO_2$), potentially accompanied by second phases. Our DFT calculation demonstrate that both cases, namely LNO + LZO and Zr-doped LNO (+ second phase) are energetically favoured over the precursor materials. We proposed several chemical reactions pathways for Zr-concentrations ranging from 1% up to 7%. The results suggest that low amounts (1-3%) of Zr can be incorporated into LNO if a Ni-rich secondary phase is also present. For higher Zr concentrations (4%), stabilization within LNO requires an oxygen-rich environment, such as high partial oxygen pressure during synthesis. This observation holds true even for elevated synthesis temperatures (~ 750°C) as confirmed by ab-initio thermodynamic calculations. At Zr concentrations above 4%, we find phase separation into LNO and LZO rather than Zr doped LNO. This phase separation is likely detrimental, as LZO exhibits a large band gap (> 5 eV), whereas 3% Zr-doped LNO and pure LNO have significantly lower band gaps (~0.2 eV and 0.4 eV respectively). Electrostatic calculation for large particle-like atomistic structures with more than 3000 atoms further reveal that Zr-doped LNO is energetically more stable in elongated particle geometries compared to spherical ones. Additionally, Zr ions tend to stay segregate towards the particle surface. This preference could explain experimental observations of elongated primary particles in Zr-doped LNO and may correlate with improved mechanical integrity and enhanced capacity retention.

In summary, this study provides theoretical insights into the synthesis challenges and structural advantages of Zr doping into LNO cathode materials. Our results indicate that Zr concentrations between 1-4% can be successfully incorporated under appropriate conditions, such as Ni-rich secondary phases or high oxygen partial pressure. These findings support the potential of Zr as a stabilizing dopant that retains the high capacity of LNO, offering guidance for future experimental efforts to further understand and develop advanced cathode materials for Li-ion batteries.