What dominates performance: synthetic method or doping strategy?

Investigating the cycling stability of doped LNMO cathodes produced via solid-state synthesis.

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1 Abstract

- Spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathode materials offer high operating voltage, high-rate capability, high energy density, low-cost and environmental benefits being Co free. Despite this, high-capacity decay challenges commercial use. Elemental doping is employed to improve stability of LNMO, and in-turn improve capacity retention.[1][2]
- In this study, solid-state method is used to synthesise $LiNi_{0.5-x}Mn_{1.5}M_xO_4$ (M = Mg, Fe. X=0, 0.05, 0.1), denoted as LNMO, $Mg_{0.05}$, $Mg_{0.1}$, $Fe_{0.05}$ and $Fe_{0.1}$, in-order to:
  - Observe the effects of doping on morphology, structure and electrochemical performance.
  - Compare performance between co-precipitation (previous work) and solid-state (this work) methods.

2 Motivation

- Co-precipitation with oxalic acid (previous work) shows only mild improvement in capacity retention for Fe-doped LNMO and significant improvement at low Mg concentrations, $Mg_{0.05}$ [**Figure 1**], contrary to literature. [1][2]
- Solid-state synthesis (this work) is employed to understand whether the synthetic method or doping strategy is the leading factor in capacity retention improvement.

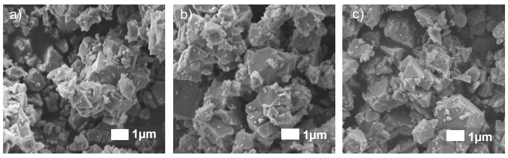

Figure 2. SEM images of a) LNMO, b) $Mg_{0.05}$ and c) $Fe_{0.05}$ via co-precipitation with oxalic acid. [3]

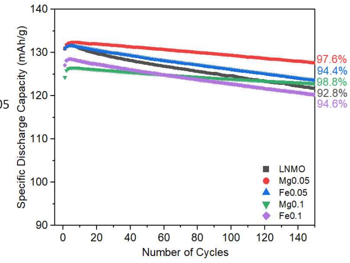

Figure 1. Specific discharge capacity retention over 150 cycles of LNMO, $Mg_{0.05}$, $Mg_{0.1}$, $Fe_{0.05}$, $Fe_{0.1}$ via co-precipitation with oxalic acid. [3]

- SEM images show that doping has no effect on material morphology via co-precipitation [**Figure 2**].

3 Scanning Electron Microscopy

- Solid-state samples are all composed of agglomerates of particles without any clear particle size uniformity.

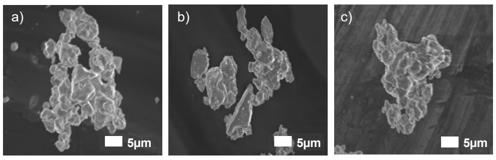

Figure 3. SEM images at 2K magnification of a) LNMO, b) $Mg_{0.05}$ and c) $Fe_{0.05}$ via solid-state synthesis.

- In comparison, co-precipitation has uniform crystalline polyhedral morphology of 1-2 μm [**Figure 2**].
- Choice of synthetic method determines material morphology.
- Choice of dopant or dopant concentration has no effect on morphology [**Figure 3**].

4 X-Ray Diffraction

- All samples display XRD pattern corresponding to $LiNi_{0.5}Mn_{1.5}O_4$ spinel structure with Fd$\bar{3}$m space group.[1]
- Presence of $Li_xNi_{1-x}O$ impurity in all samples [**Figure 4**].[1] [2]
- Impurity concentration decreases with increasing Fe concentration whilst Mg forms additional Li_2MnO_3 impurity at x=0.1 [**Figure 4**].

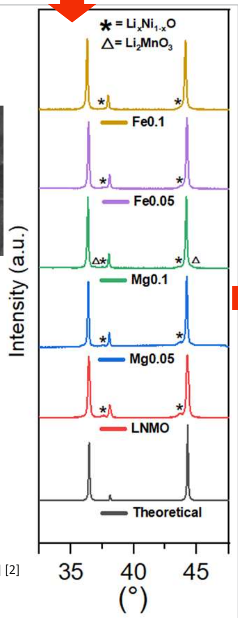

Figure 4. XRD patterns of LNMO, $Mg_{0.05/0.1}$ and $Fe_{0.05/0.1}$, over a selected 2θ range to highlight impurity peaks.

5 Electrochemistry

- Charge/Discharge curves show that initial discharge capacity decreases when X > 0.05 [**Figure 7**].
- Doping causes an increase in 4 V capacity with increasing dopant concentrations suggesting an increase in Mn^{3+} concentration [**Figure 5-6**].
- Decrease in 4.75 V capacity with increasing concentration due to decrease in Ni^{2+} concentration [**Figure 5-6**].[1]

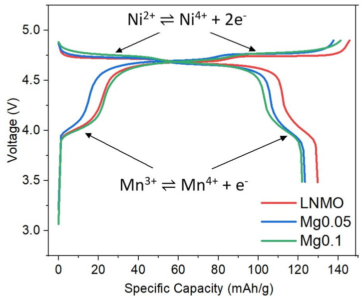

Figure 5. First charge/discharge curve of LNMO, $Mg_{0.05}$ and $Mg_{0.1}$.

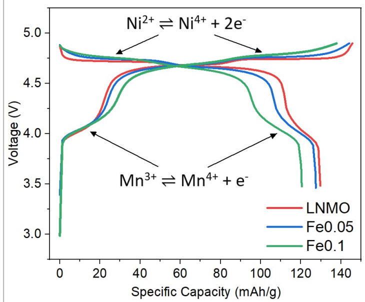

Figure 6. First charge/discharge curve of LNMO, $Fe_{0.05}$ and $Fe_{0.1}$.

- Over 150 cycles, capacity retention increases from LNMO (88.1%) to $Fe_{0.05}$ (94.0%) to $Fe_{0.1}$ (96.0%) [**Figure 6**].
- Capacity retention has no change with $Mg_{0.05}$ doping but improves with $Mg_{0.1}$ from 88.1% to 96.4% over 150 cycles [**Figure 5**].
- Capacity retention of solid-state LNMO over 150 cycles is 88.1% compared to 92.8% achieved by co-precipitation method, attributed to change in morphology [**Figure 1 and 5**].
- Solid-state $Mg_{0.05}$ shows no change in cycling stability, whereas with co-precipitation $Mg_{0.05}$ capacity retention increases by 4.9% and retains initial capacity [**Figure 1 and 5**].

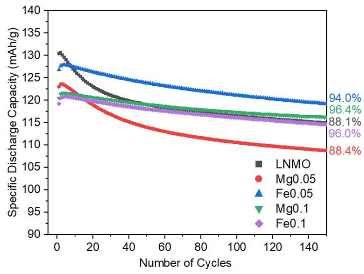

Figure 7. Specific Discharge Capacity retention over 150 cycles of LNMO, $Mg_{0.05}$, Mg0.1, $Fe_{0.05}$, $Fe_{0.1}$ via solid-state synthesis.

6 Conclusions

- Doping improves capacity retention when X > 0.05 for Mg and X ≥ 0.05 for Fe.
- Unlike co-precipitation which shows improvement in capacity retention to be independent of dopant concentration, solid-state shows concentration dependency.
- Synthetic method is the dominant factor in improving capacity retention of Mg doped materials. However, capacity retention of Fe doped materials is independent of the synthetic method used.

7 Impact / Next steps

- This work can act as a baseline with which to compare performance effects of doping on LNMO between synthetic methods.
- More stark improvements in capacity and capacity retention of co-precipitation needs to be weighed up against potential increase in cost and energy use to determine optimal method.
- Resynthesize materials via other synthetic techniques to compare them.

8 Method

- Spinel $LiNi_{0.5-x}Mn_{1.5}M_xO_4$ (M = Mg, Fe. X=0, 0.05, 0.1) synthesised by ball-milling-stoichiometric amounts of Li_2CO_3, NiO, MnO_2 and MgO/Fe_3O_2 at 300 rpm for 12 hours followed by sintering at 850°C for 10 hours.[1]
- Electrodes (150 μm x 12 mm) prepared by mixing Active Material:Carbon Black:PVDF in 80:10:10 ratio in N-methyl-2-pyrrolidone (NMP), cast on Al foil, and dried under vacuum at 120°C for 12 hours.
- Spinel/Li half-cells made using 10 mm Li-chips and 120 μl $LiPF_6$ in EC/DMC (1:1, V:V) electrolyte.
- Electrochemical cycling at 1C (3.5-4.9 V) and 50°C to promote degradation.

Intern bio

Jacob is a 2nd year MSci Chemistry student at Imperial College London. Interested in synthetic organic and inorganic chemistry.

9 References

[1]. G. Liang, Z. Wu, C. Didier, W. Zhang, J. Cuan, B. Li, K.-Y. Ko, P.-Y. Hung, C.-Z. Lu, Y. Chen, G. Leniec, S. M. Kaczmarek, B. Johannessen, L. Thomsen, V. K. Peterson, W. K. Pang and Z. Guo, *Angewandte Chemie International Edition*, 2020, **59**, 10594–10602.

[2] J. Liu and A. Manthiram, *The Journal of Physical Chemistry C*, 2009, **113**, 15073–15079

[3]. Murdock, B., Fitzpatrick, J. Menon, A., Booth, S., Kumar, P. Lee, T. Tapia-Riuz N. Revealing the correlation between surface and performance in LiNi0.45M0.05Mn1.5O4 (M=Fe, Mg) cathode materials for lithium-ion batteries. ***In progress.***

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