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In situ Synchrotron Diffraction Studies on $LiNi_{0.5}Mn_{1.5}O_4$ and also Fe substituted $LiNi_{0.5}Mn_{1.5}O_4$ Spinel Cathodes during Electrochemical Cycling

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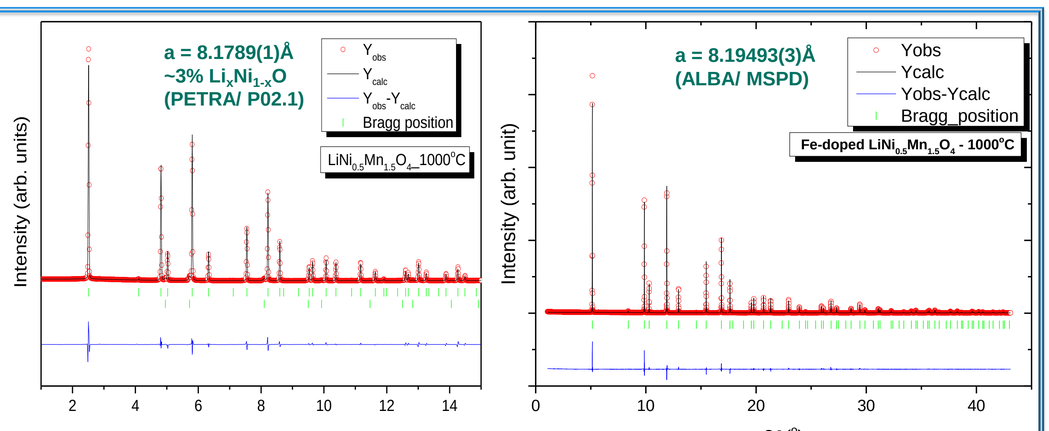
INTRODUCTION

The spinel $LiNi_{0.5}Mn_{1.5}O_4$ cathode shows impressive electrochemical performance like large reversible capacity at a high operating voltage around 4.7 V where the reversible $Ni^{2+} \leftrightarrow Ni^{4+}$ redox reactions take place which makes it a promising and suitable cathode material for high energy battery applications [1]. However, the electrochemical performance of spinel $LiNi_{0.5}Mn_{1.5}O_4$ still needs to be improved to meet the required power density especially at high charge/discharge rates (C-rates) and at elevated temperatures. Cationic doping such as Fe on $LiNi_{0.5}Mn_{1.5}O_4$ is one of the techniques to improve the electrochemical performance. It has been reported that Fe doping exhibits a better electrochemical performance than $LiNi_{0.5}Mn_{1.5}O_4$ [2] and gives better thermal stability [3]. Therefore, the multiple substitution of Fe for Ni and Mn ($LiFe_{0.2}Ni_{0.4}Mn_{1.4}O_4$) on the crystallographically interesting transition metal sites 16*d* will be investigated.

RESULTS

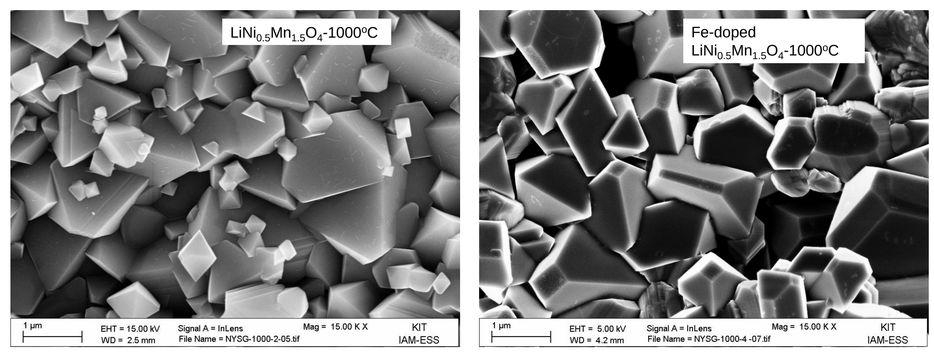
***Synchrotron Diffraction* :** *Ex situ* and *in situ* X-ray diffraction experiments were carried out at the High Resolution Powder Diffraction Beam Line (P02.1) at PETRA-III, DESY, using synchrotron radiation with an energy of 60 keV (λ=0.207260 Å) and at the Materials Science and Powder Diffraction Beam Line (MSPD) in ALBA using synchrotron radiation with an energy of 30 keV (λ=0.42477 Å). The detector in P02.1 beam line is a 2D flat panel detector (Perkin Elmer amorphous-Silicon detector) and in MSPD beam line is MYTHEN 1D Position Sensitive.

Rietveld Refinement



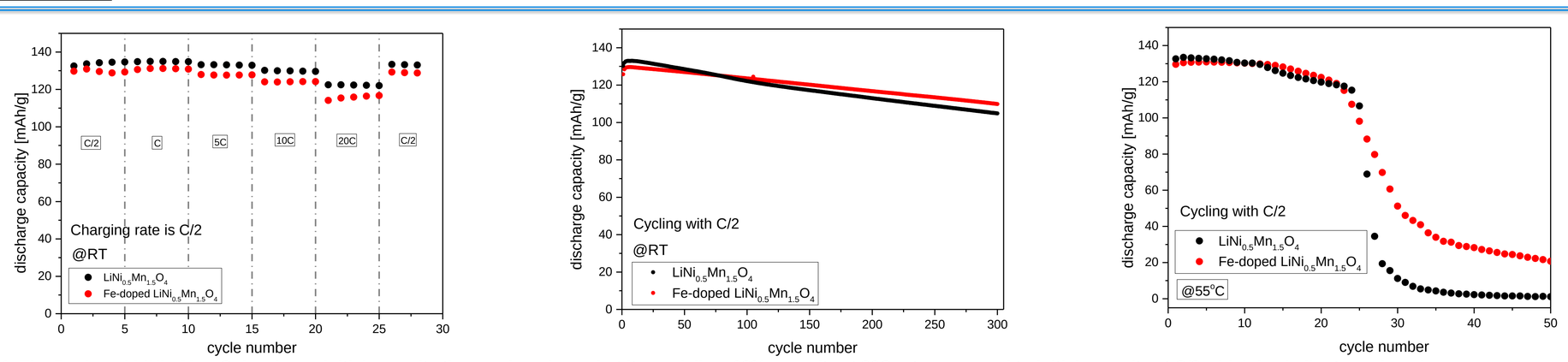
→ *The impurity phase ($Li_xNi_{1-x}O$) vanishes after Fe-doping on $LiNi_{0.5}Mn_{1.5}O_4$.*

SEM images



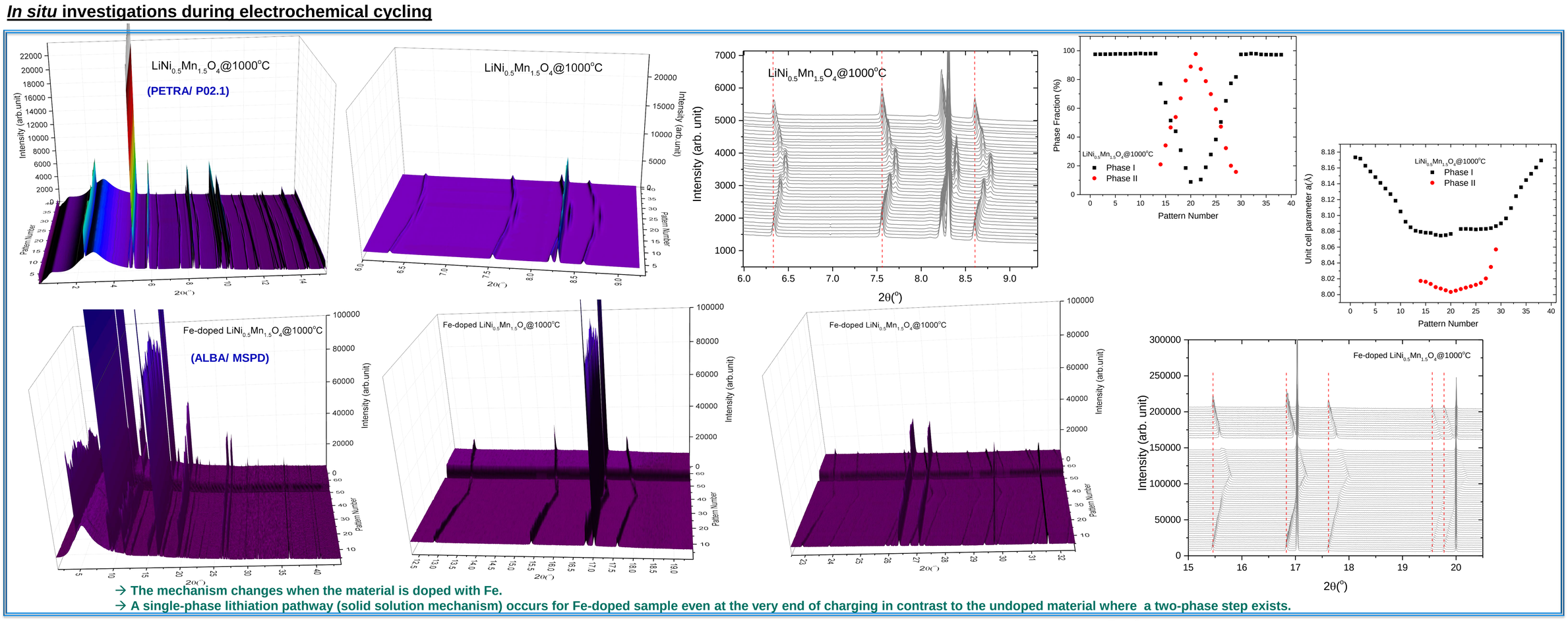
→ *The particles are well shaped for both materials ($LiNi_{0.5}Mn_{1.5}O_4$ and Fe-doped $LiNi_{0.5}Mn_{1.5}O_4$) and have high crystallinity.*

Electrochemical Performances



→ *The Fe-doped $LiNi_{0.5}Mn_{1.5}O_4$ has lower initial capacity than undoped one, but it can deliver 92% capacity at 20C rate compared to initial capacity at C/2 which is similar to undoped one.*
→ *The capacity retention at RT after 300 cycles is higher for Fe-doped $LiNi_{0.5}Mn_{1.5}O_4$ than the undoped one.*

In situ investigations during electrochemical cycling



→ **The mechanism changes when the material is doped with Fe.**
→ **A single-phase lithiation pathway (solid solution mechanism) occurs for Fe-doped sample even at the very end of charging in contrast to the undoped material where a two-phase step exists.**

Conclusion

- $LiNi_{0.5}Mn_{1.5}O_4$ contains small amounts of $Li_xNi_{1-x}O_4$ impurity which has been vanished after Fe-doping.
- Even though Fe-doped sample has lower initial capacity than undoped one, it has better capacity retention after 300 cycles (*$LiNi_{0.5}Mn_{1.5}O_4$ has 79,5% and Fe-doped has 87,3%)*.
- The structural mechanism occurred during electrochemical cycling is reversible for both samples. Additionally an intermediate phase (2nd main phase ($Fd\bar{3}m$)) appears at ~4.7 V for $LiNi_{0.5}Mn_{1.5}O_4$, on both charging & discharging processes where Ni^{2+}/ Ni^{4+} electrochemical reaction takes place [1] which is not observed after Fe-doping.

Acknowledgement

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References

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