

# Lithium manganese orthosilicate cathode material for Li-ion batteries: synthesis, characterization and electrochemical behaviour

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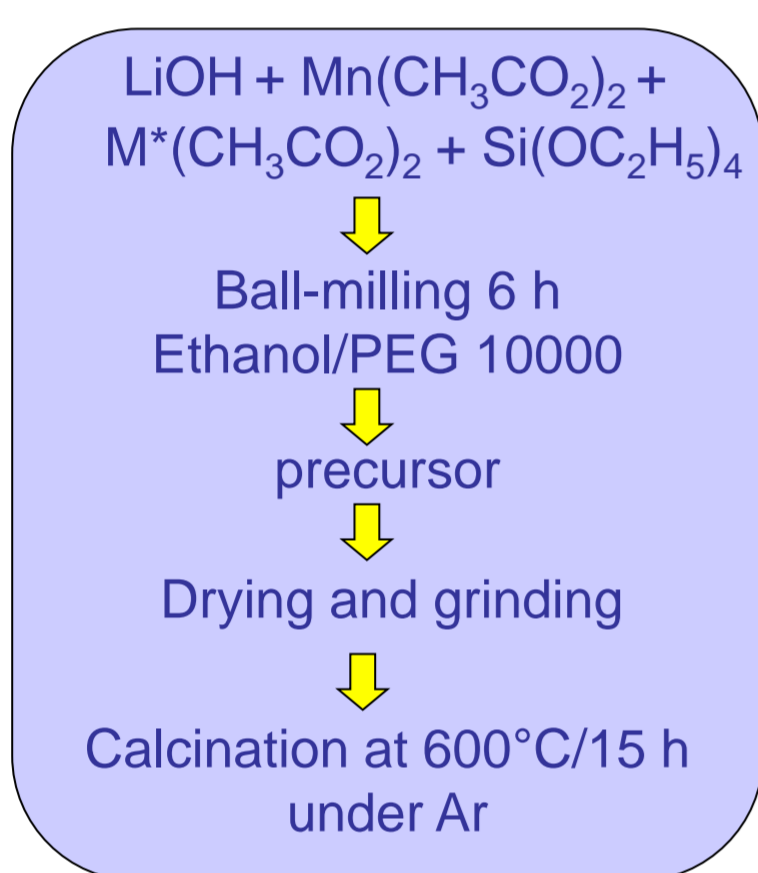
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## Introduction

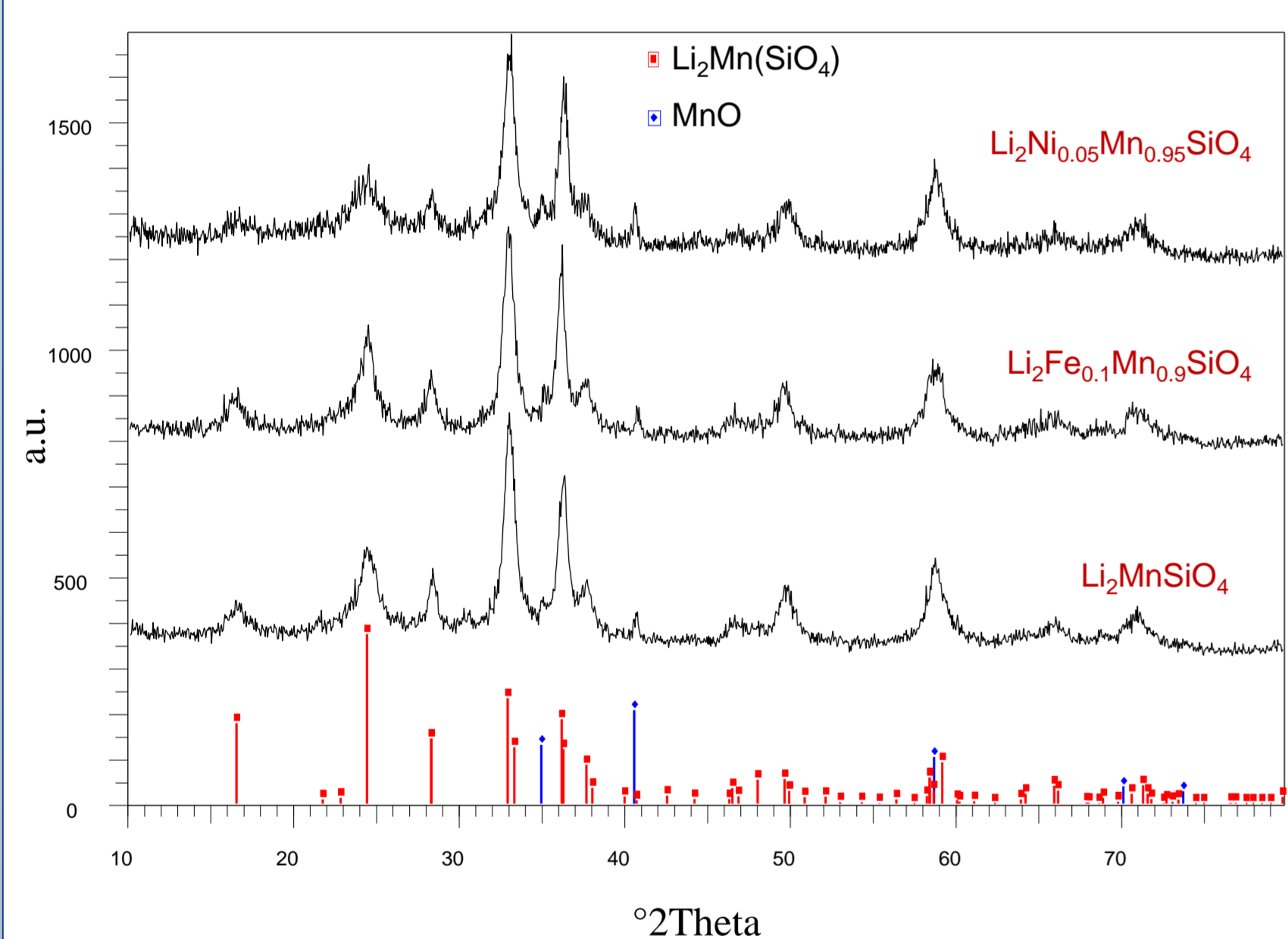
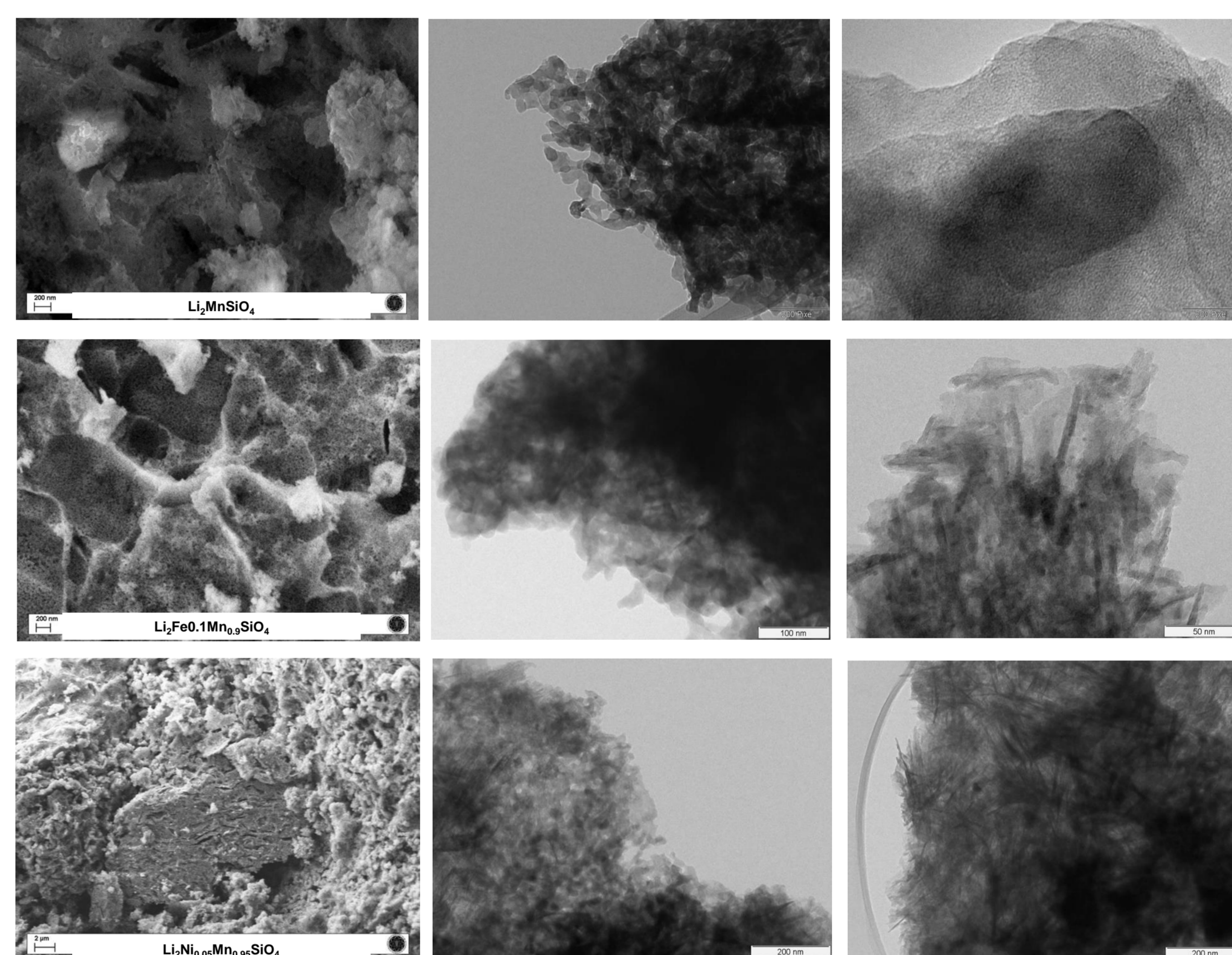
To increase the energy density of Li-ion batteries, new classes of cathode materials with improved characteristics in terms of specific capacity, cost and safety are needed. The orthosilicate  $\text{Li}_2\text{MSiO}_4$  (M=Fe, Mn, Co, Ni) family is attractive due to the theoretical possibility of exchanging two  $\text{Li}^+$  per formula unit and to the higher thermal stability with respect to layered and spinel-like oxide cathode materials [1]. Dilithium manganese orthosilicate  $\text{Li}_2\text{MnSiO}_4$  undergoes to amorphisation during the first electrochemical charge that translates into drastic capacity fading [2]. The low intrinsic conductivity of silicates can be improved by carbon coating and by the reduction of the particle size. Here we report the characterization of carbon coated  $\text{Li}_2\text{MnSiO}_4$  and  $\text{Li}_2\text{M}_x\text{Mn}_{(1-x)}\text{SiO}_4$  (M=Fe or Ni) structures synthesized by a PEG-assisted solid state route [3].

## Synthesis and Characterization



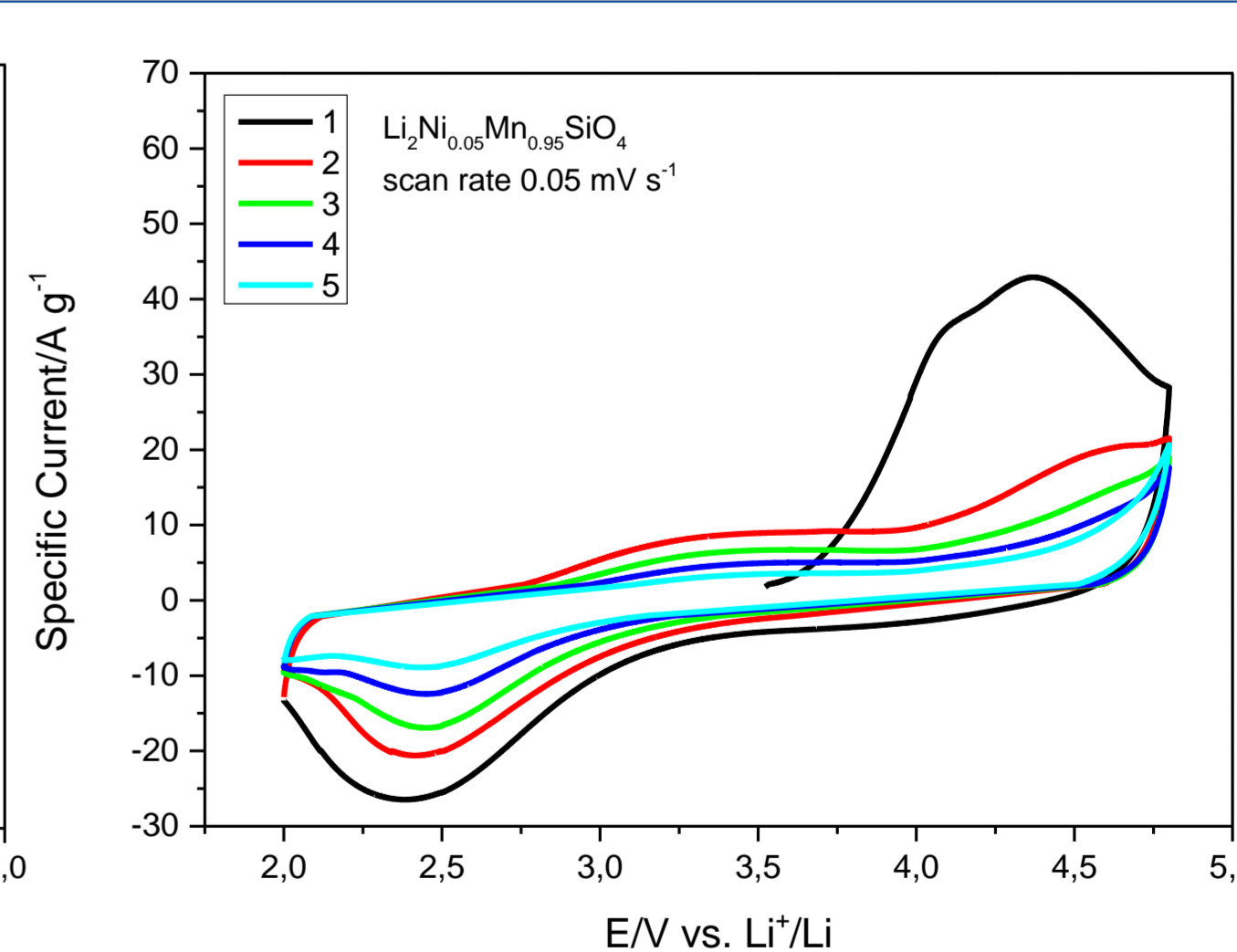
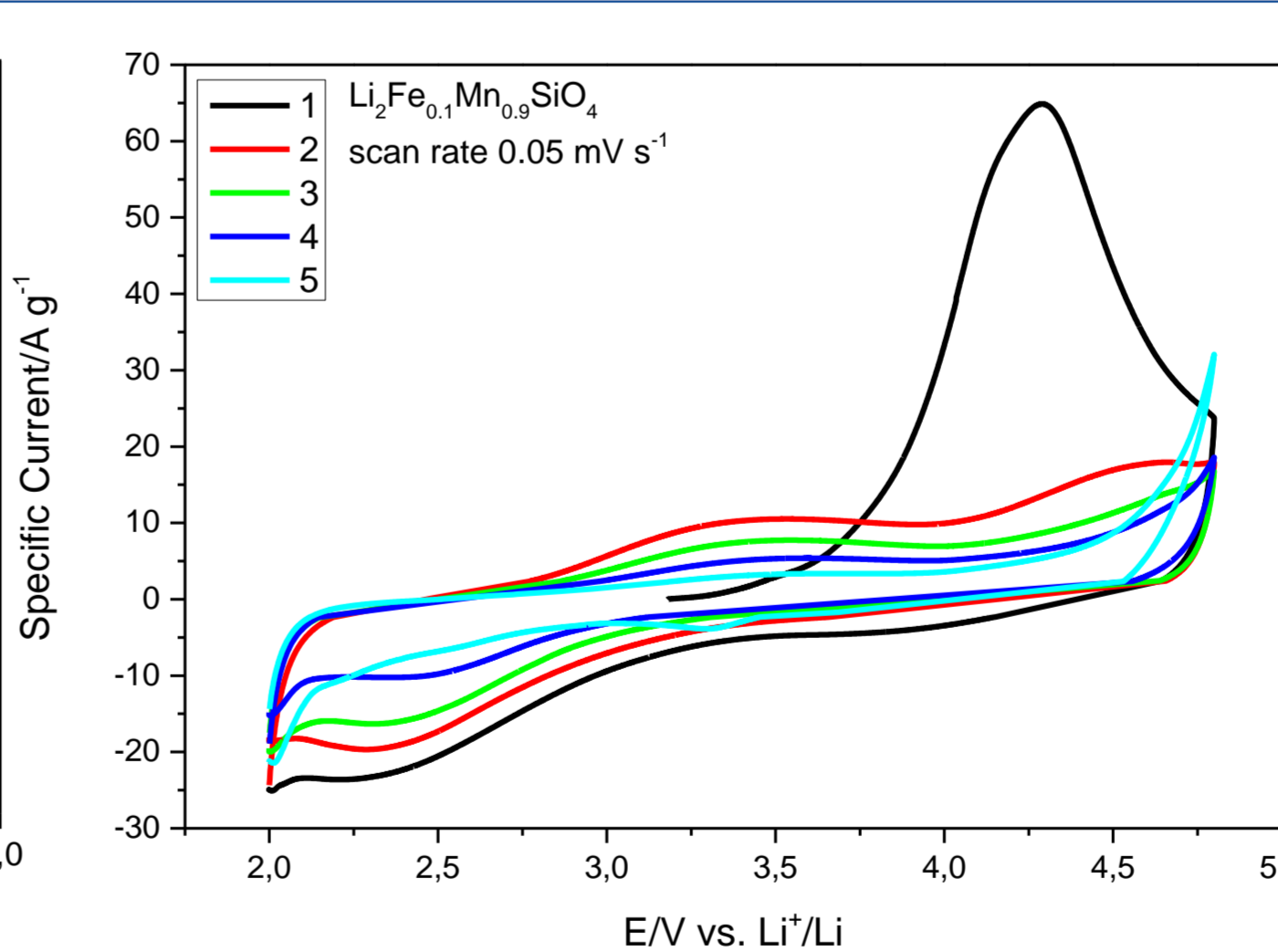
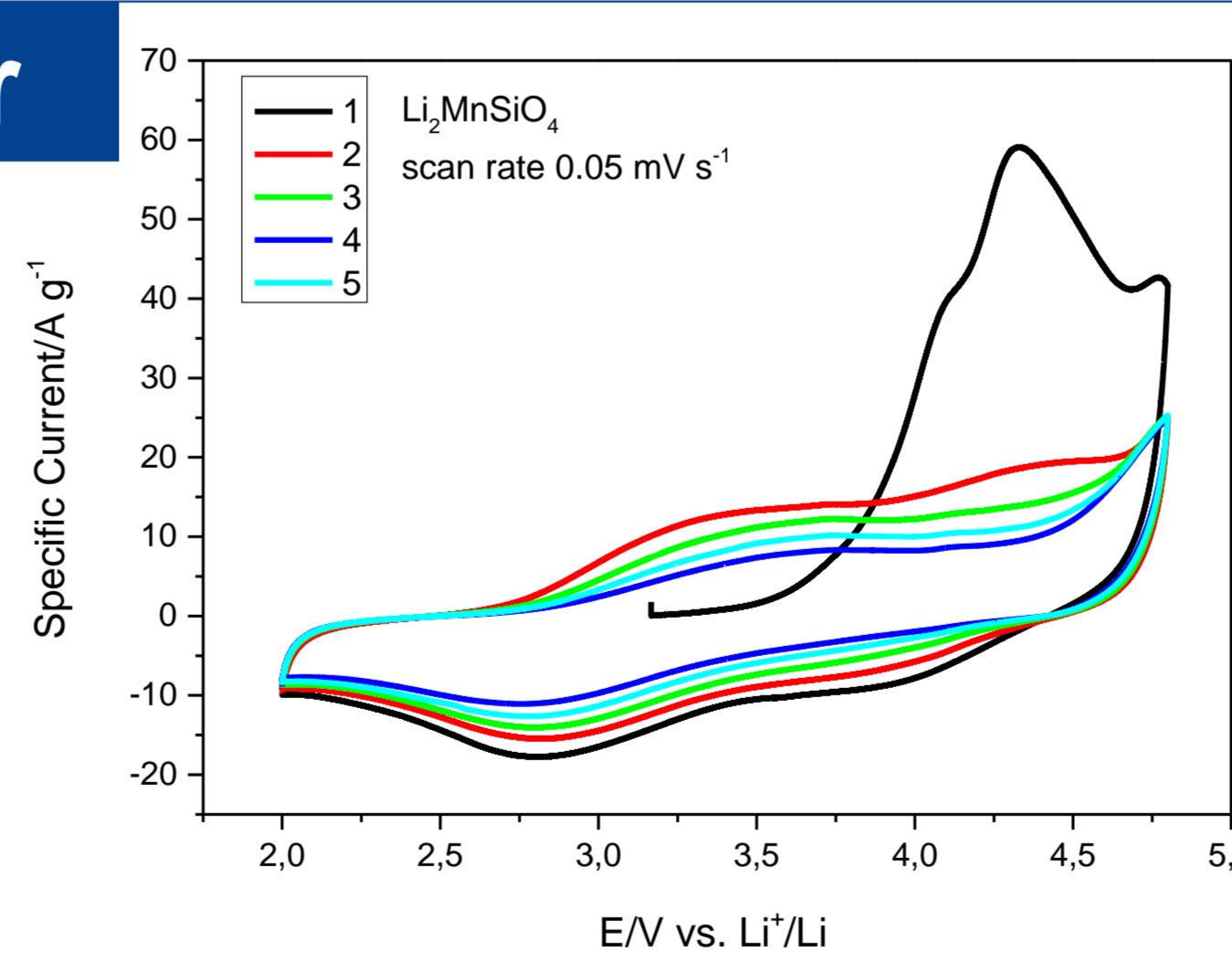
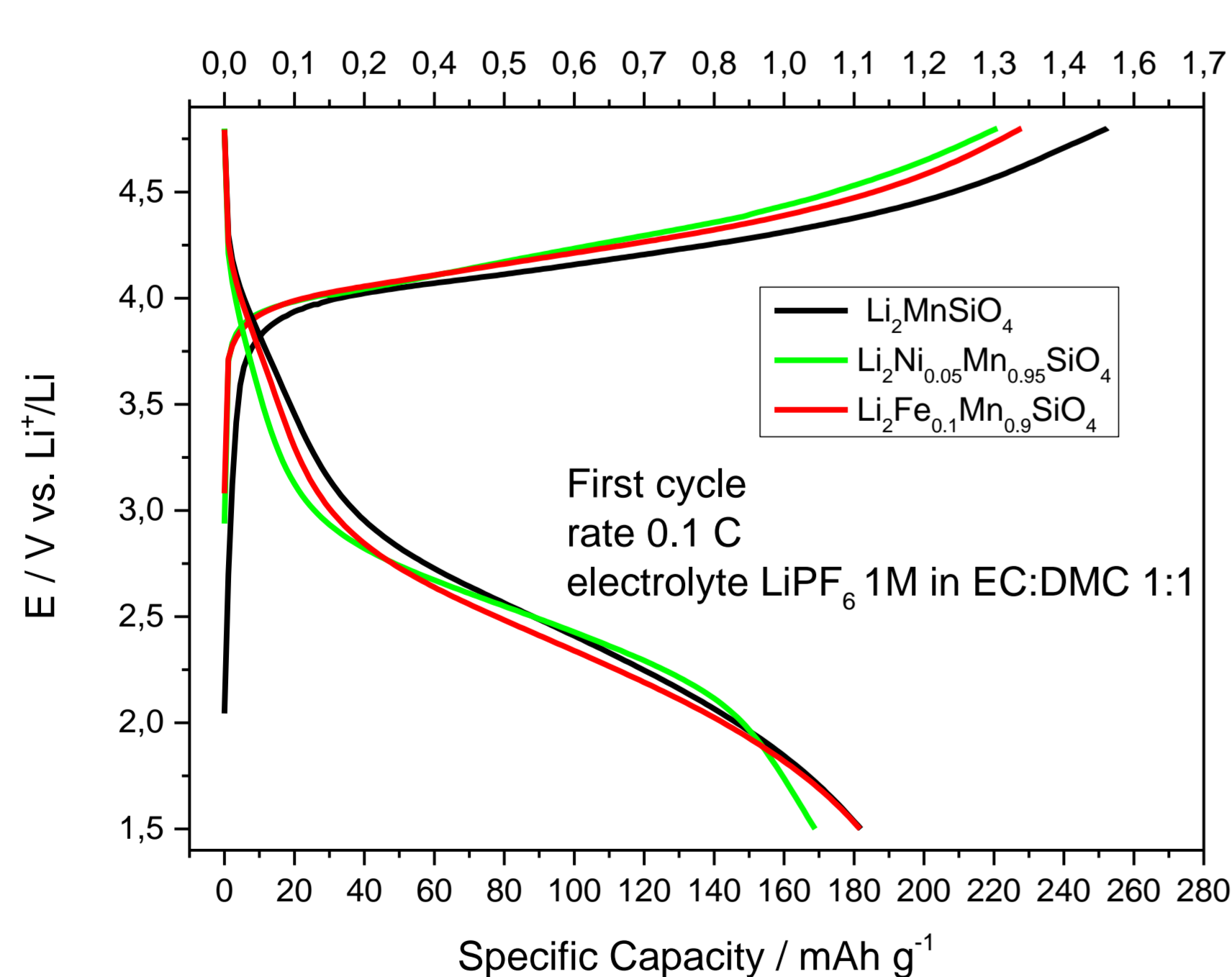
\*M=Fe or Ni

Sample	$\text{Li}_2\text{MnSiO}_4$	$\text{Li}_2\text{Fe}_{0.1}\text{Mn}_{0.9}\text{SiO}_4$	$\text{Li}_2\text{Ni}_{0.05}\text{Mn}_{0.95}\text{SiO}_4$
Phase identification /impurities	$\text{Li}_2\text{MnSiO}_4$ / MnO	$\text{Li}_2\text{Fe}_x\text{Mn}_{(1-x)}\text{SiO}_4$ / MnO	$\text{Li}_2\text{Ni}_x\text{Mn}_{(1-x)}\text{SiO}_4$ / MnO
Space group	$Pmn2_1$	$Pmn2_1$	$Pmn2_1$
lattice parameters (XRD)	a: 6.308(21) b: 5.408(24) c: 4.974(19)	a: 6.304(20) b: 5.396(22) c: 4.978(19)	a: 6.303(34) b: 5.424(29) c: 4.963(28)
Crystal size (XRD)	10.8(12) nm	11.7(16) nm	10.3(32) nm
carbon coating (%)	4.7	5.1	5.8



- nano-sized particles with  $Pmn2_1$  crystal structure and ~5% MnO (impurity)
- ~ 5% carbon coating (detected by Elemental Analysis)
- high porous materials partially amorphous needle-like morphology for the Ni- and Fe-containing samples
- changes in the lattice parameters likely due to the insertion of Ni or Fe

## Electrochemical behaviour



- High discharge capacity during the first cycle at 0.1C rate in standard electrolyte
- All the structures show rapid capacity fading
- Ni- and Fe-containing material shows slightly different electrochemical behaviour on galvanostatic profile and cyclic voltammogram: this suggests possible influence on the  $\text{Li}^+$  insertion/extraction mechanism

## Conclusions

Nano-sized, carbon coated  $\text{Li}_2\text{MnSiO}_4$  and partially substituted  $\text{Li}_2\text{M}_x\text{Mn}_{(1-x)}\text{SiO}_4$  (M=Fe or Ni) structures with  $Pmn2_1$  space group have been successfully synthesized by solid state route. Despite the amount of Ni or Fe is too small to increase electrochemical performances, the electrochemical characterization shows some differences due to the presence of the metals. Further experiments are under progress to clarify the effect on the  $\text{Li}^+$  insertion/extraction mechanism.

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### References

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