

Nano-structured lithium manganese phosphate via solvothermal reaction and anion substitution

Lars Esmezjan^[a], Sylvio Indris^[a], Maximilian Kaus^[a], Vanessa Trouillet^[a], Murat Yavuz^[a, b], Helmut Ehrenberg^[a, b]

^[a]Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM)-Energy Storage Systems (ESS)

^[b]Helmholtz Institute of Ulm (HIU) Electrochemical Energy Storage, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Introduction

Lithium-ion batteries are commonly built with LiCoO₂ as cathode material. However, there are still some issues that need to be improved like toxicity and safety [1]. Thus, new cathode materials were developed. Among them, the olivine-type orthophosphates LiMPO₄ (with M = Fe, Mn, Co, Ni) attract much attention. They have an orthorhombic structure with space group Pmnb. Tetrahedral vacancies are occupied by phosphorus and octahedral vacancies by lithium and the transition metal [2]. The lithium diffusion takes place in 1D-diffusion paths along the a-axis (Fig. 1). Depending on the used metal M the material has operation voltages of 3.5 V (LiFePO₄), 4.1 V (LiMnPO₄), 4.8 V (LiCoPO₄) and 5.1 V (LiNiPO₄) vs Li/Li⁺ [3]. Nevertheless, LiMnPO₄ shows the highest value with regard to the stability window of the commercial used electrolytes. Further advantages of this material are the abundance of the elements in the earth's crust, better safety characteristics and lower toxicity. The greatest disadvantage of LiMnPO₄ is the very low ionic and electronic conductivity, even worse compared to the iron compound. This leads to a sluggish kinetic and poor rate capability [4]. To overcome these drawbacks several approaches have been established in literature:

- synthesis of nanoparticles to get shorter diffusion paths [5],
- carbon coating of the active material to enhance the conductivity [6],
- doping of the material with different metals [7].

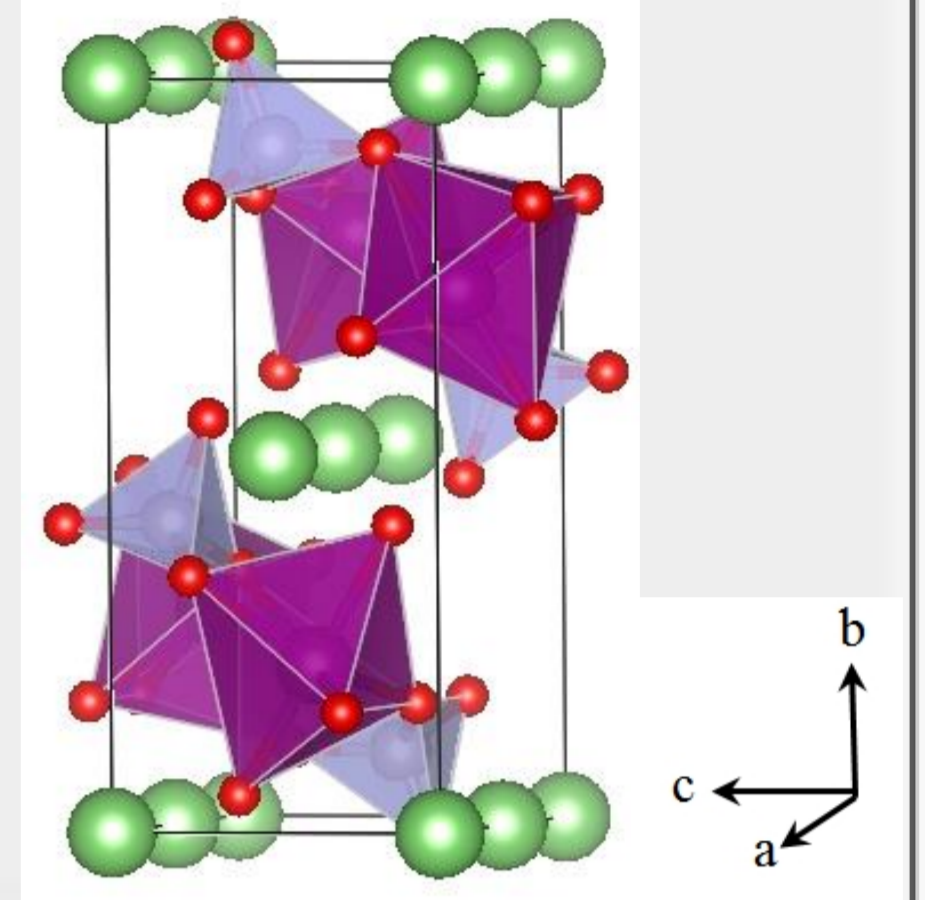


Fig. 1: Olivine structure (Pmnb) of LiMnPO₄ with MnO₆-octahedron, PO₄-tetrahedron and lithium diffusion path; atom colours: Li (green), Mn (purple), P (blue) and O (red).

Experimental Details

Synthesis:

Nano-structured LiMnPO₄ and doped LiMn(PO₄)_{0.9}(MO₄)_{0.1} with M = V, Ti, Si were synthesized in diethylene glycol via solvothermal reaction at 200 °C (Fig.2). As precursors Mn(CH₃COO)₂, Li(CH₃COO) and H₃PO₄ were used. For substitution of the phosphate ion V₂O₅, Ti(OⁱPr)₄ or Li₄SiO₄ was added during synthesis. The as-prepared materials were then coated with carbon and annealed at 650 °C for 4 h in an Ar/H₂-atmosphere.

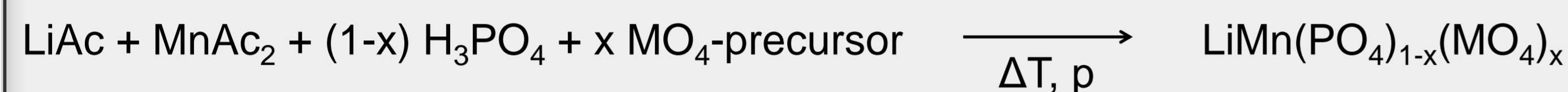


Fig. 2: Synthesis of doped LiMnPO₄.

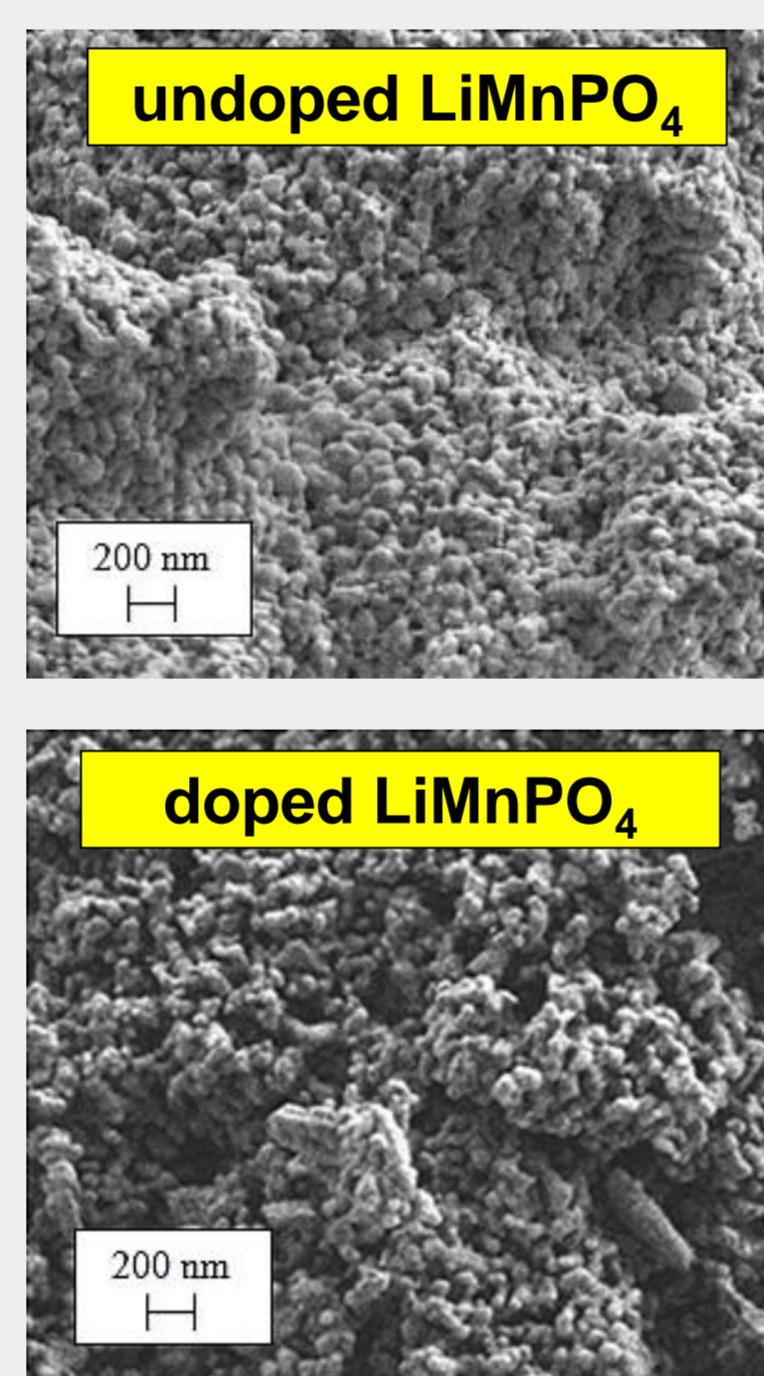
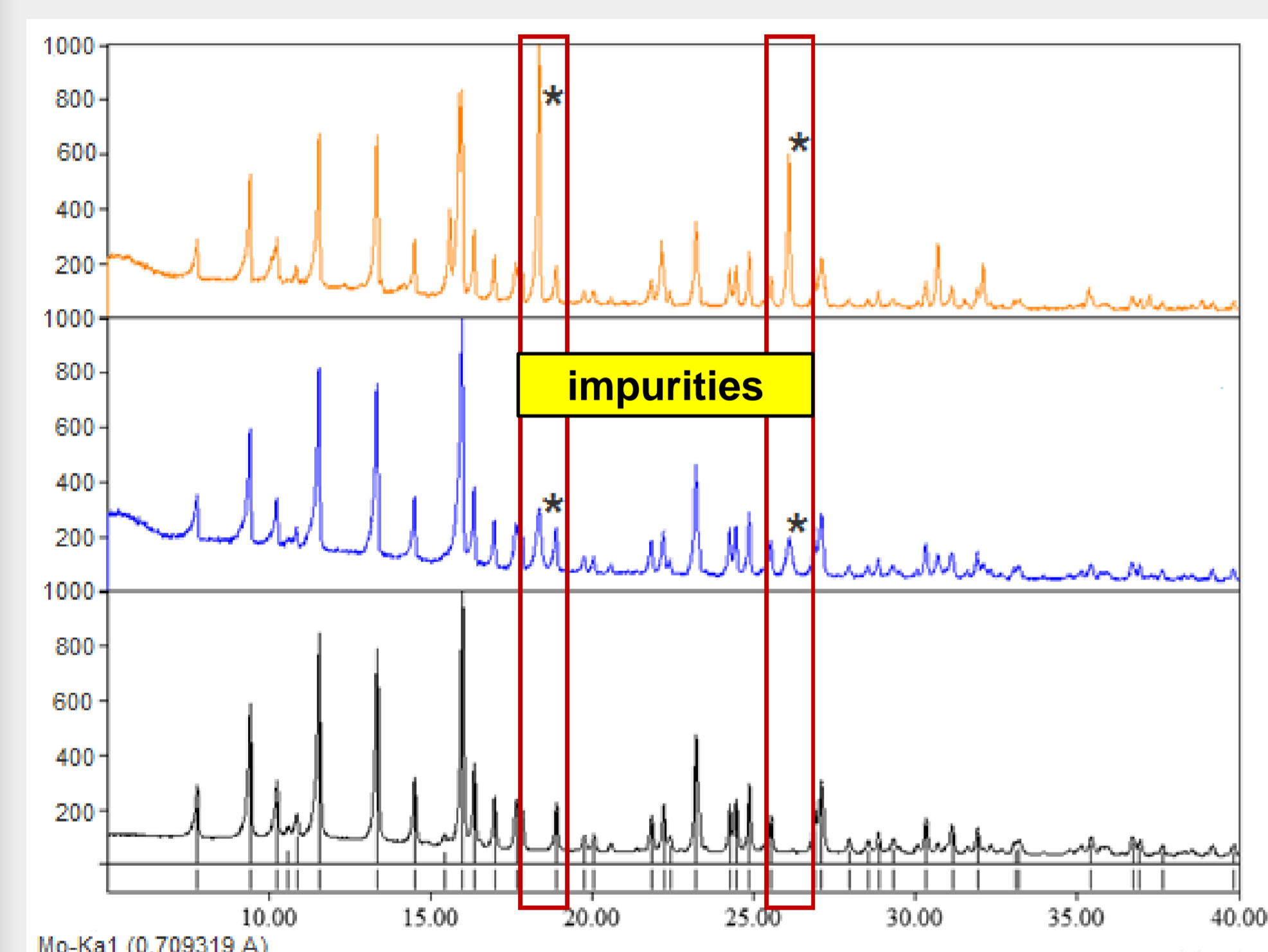
Characterization:

XRD experiments were carried out with a STOE Stadi P diffractometer (Mo-Kα1-radiation, λ = 0.70926 Å) in Debye-Scherrer mode. The morphology of the particles was studied with LEO 1530 SEM. XPS measurements were performed with a Thermo Fischer Scientific K-Alpha Spectrometer with micro-focused monochromatic-AlKα X-ray source. Charge compensation was applied with low energy electrons and Ar⁺-ions.

Electrochemical Experiments:

Electrodes were prepared by mixing the active material with Super P carbon (Timcal) and polyvinylidene fluoride (PVdF) binder (Solvay) in a weight ratio of 8:1:1. After adding 1-Methyl-2-pyrrolidinone (NMP) the slurries were coated on Al-foil and dried. The electrodes were electrochemically measured with Li metal as counter electrode on a VMP3 potentiostat (with 0.02 C, between 2,5 V and 4,6 V).

Results: Powder characterization

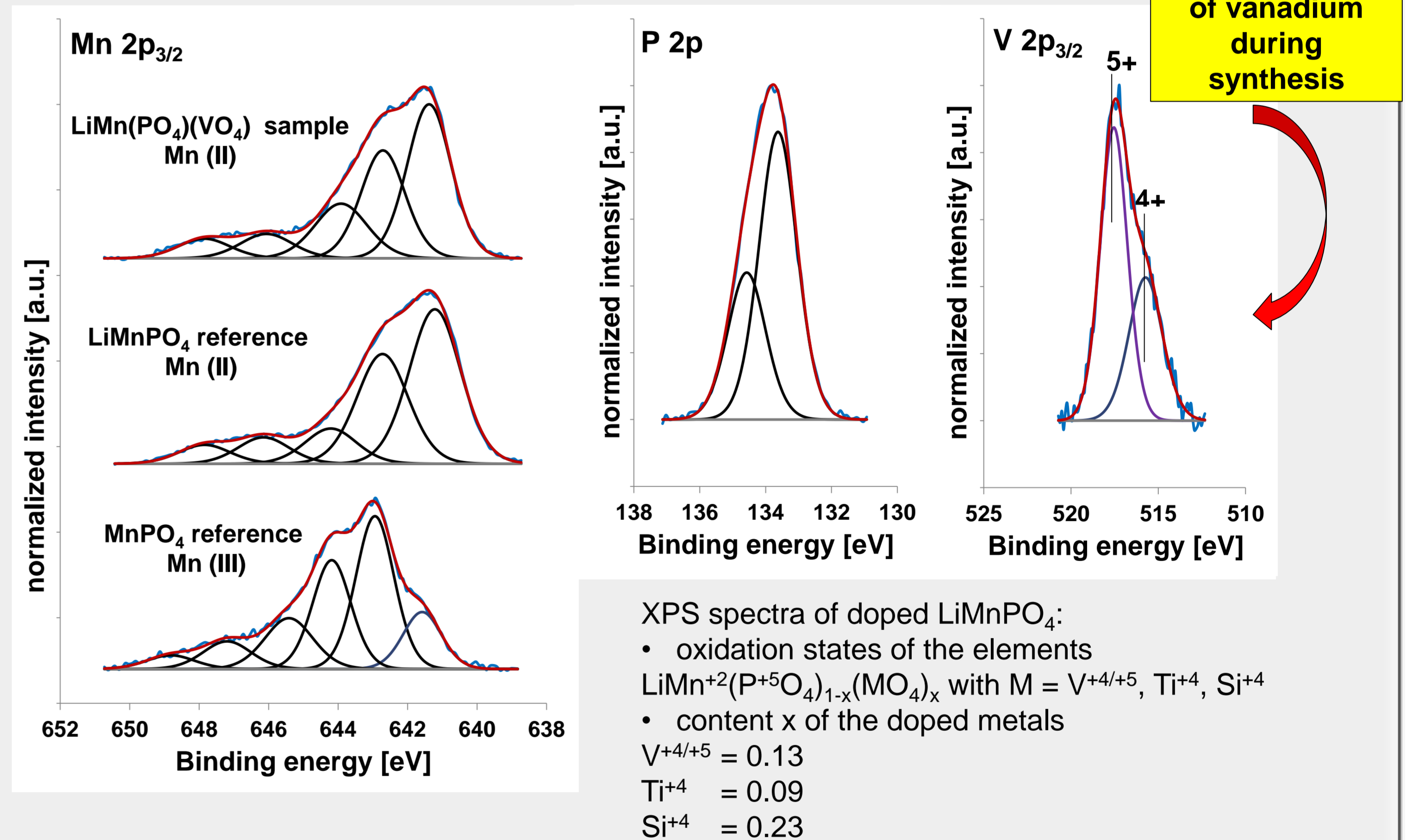


SEM images show homogeneous and nanosized particles with small size distribution

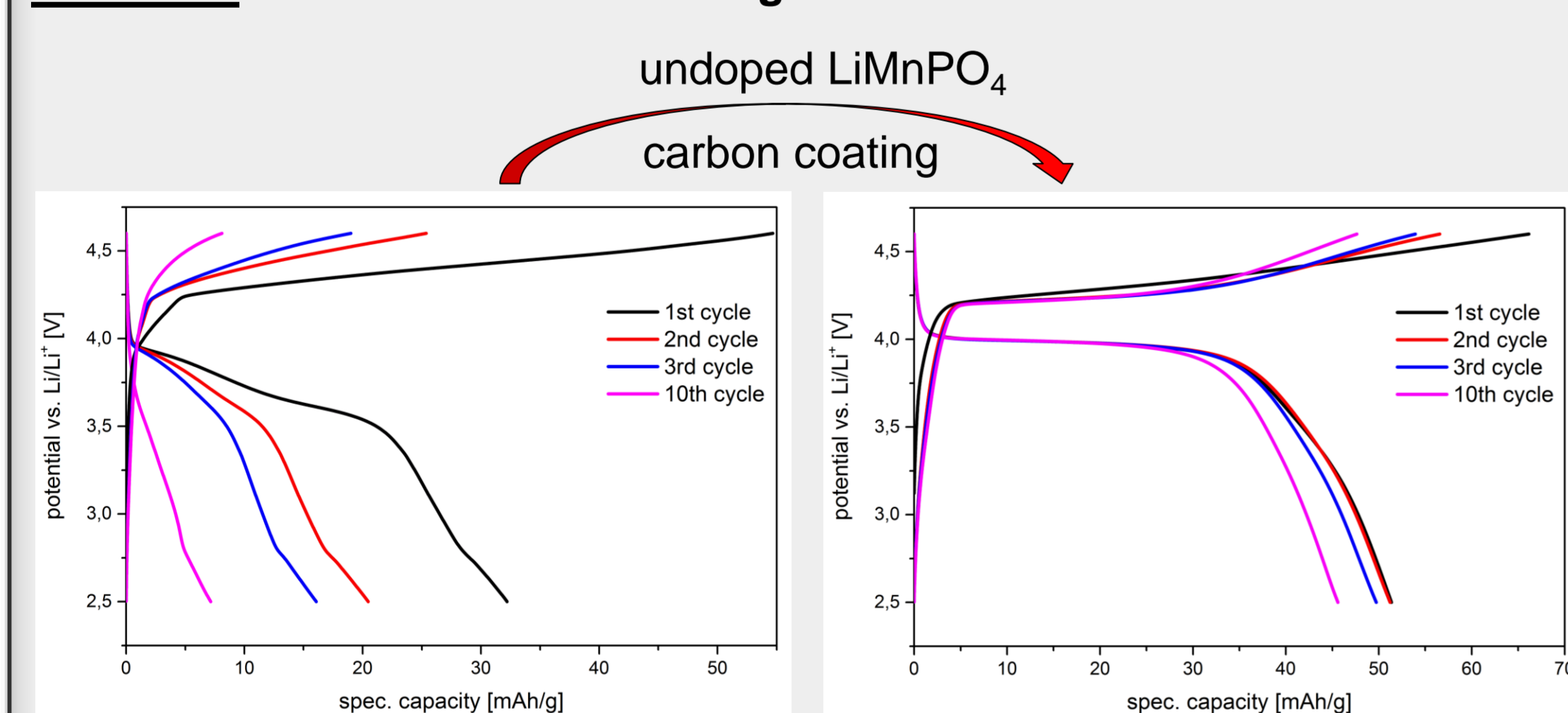
XRD pattern of as-prepared LiMnPO₄:

- impurities are marked with asterisk,
- variation of synthesis conditions led to phase-pure samples (bottom).

Results: XPS measurements



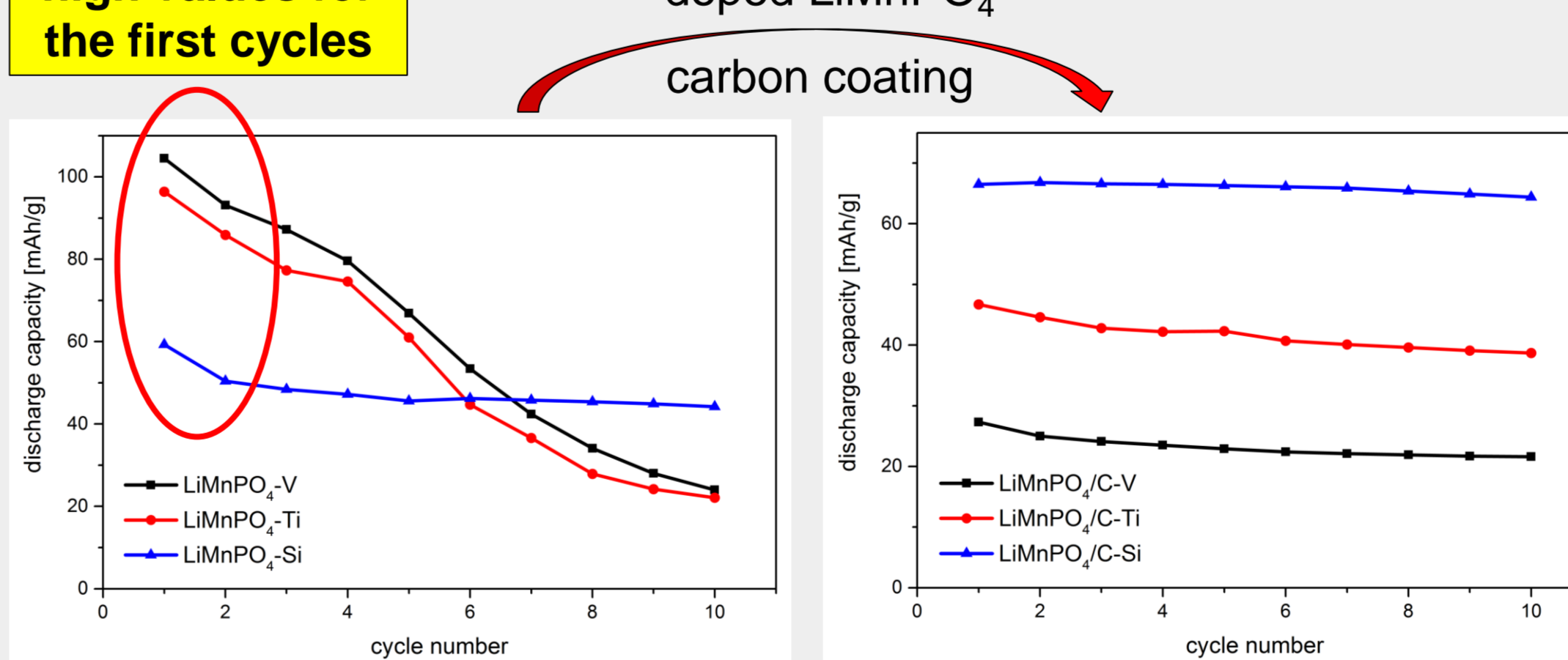
Results: Electrochemical investigations



charge/discharge cycles of undoped LiMnPO₄:

- non-coated samples vs. carbon coated samples

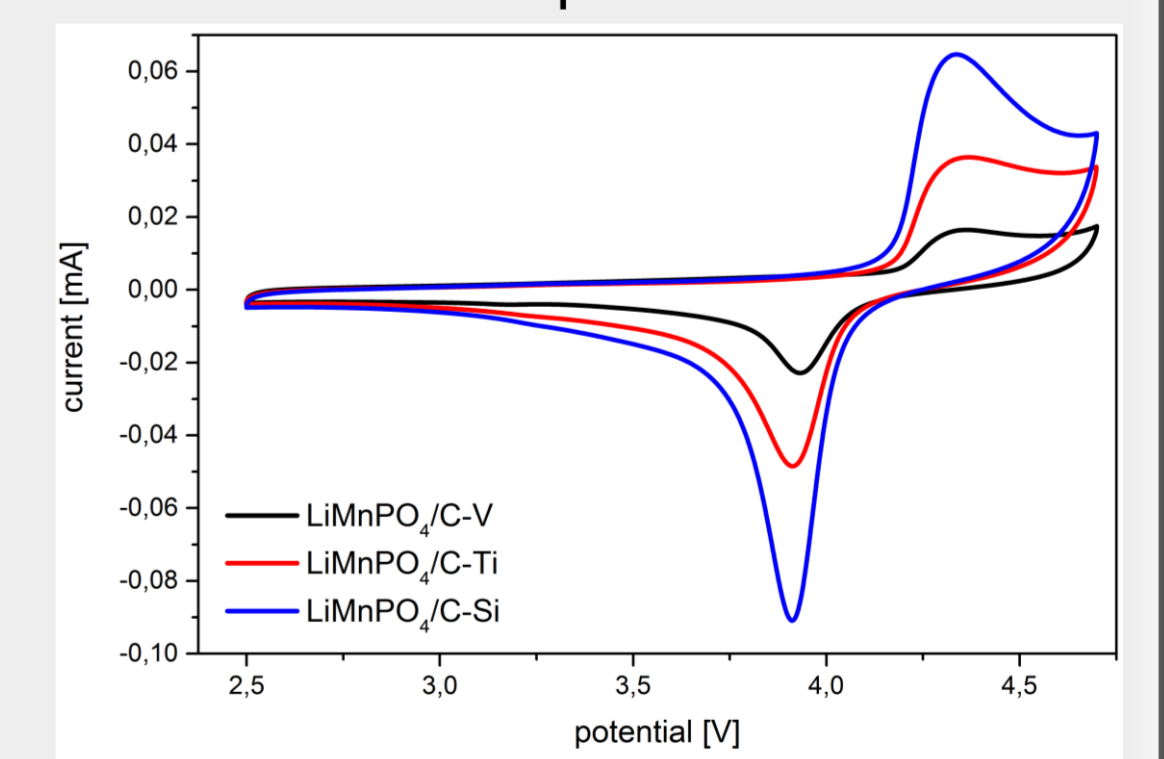
high values for the first cycles



discharge capacities of doped LiMnPO₄:

- non-coated samples vs. carbon coated samples

carbon coating + doped



CV curves of doped LiMnPO₄:

- no shift of redoxpotential (current 0,1 mV/s)

Conclusion

- phase-pure products with orthorhombic structure, space group Pmnb
- homogeneous, nanosized particles (100-300 nm)
- doping of V on Mn-site (octahedral) → cation substitution
- doping of Ti/Si on P-site (tetrahedral) → anion substitution
- with carbon coating better cycling stability
- doping enhanced discharge capacity (from 30 mAh/g up to 100 mAh/g)
- Si-doping also improved cycling stability (97 % capacity retention after 10 cycles)
- only Mn⁺²/Mn⁺³ is electrochemically active

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