

TA-DOPED POLYCRYSTALLINE NI-RICH LAYERED OXIDE CATHODES: EFFECTS ON MORPHOLOGY AND ELECTROCHEMICAL PERFORMANCE

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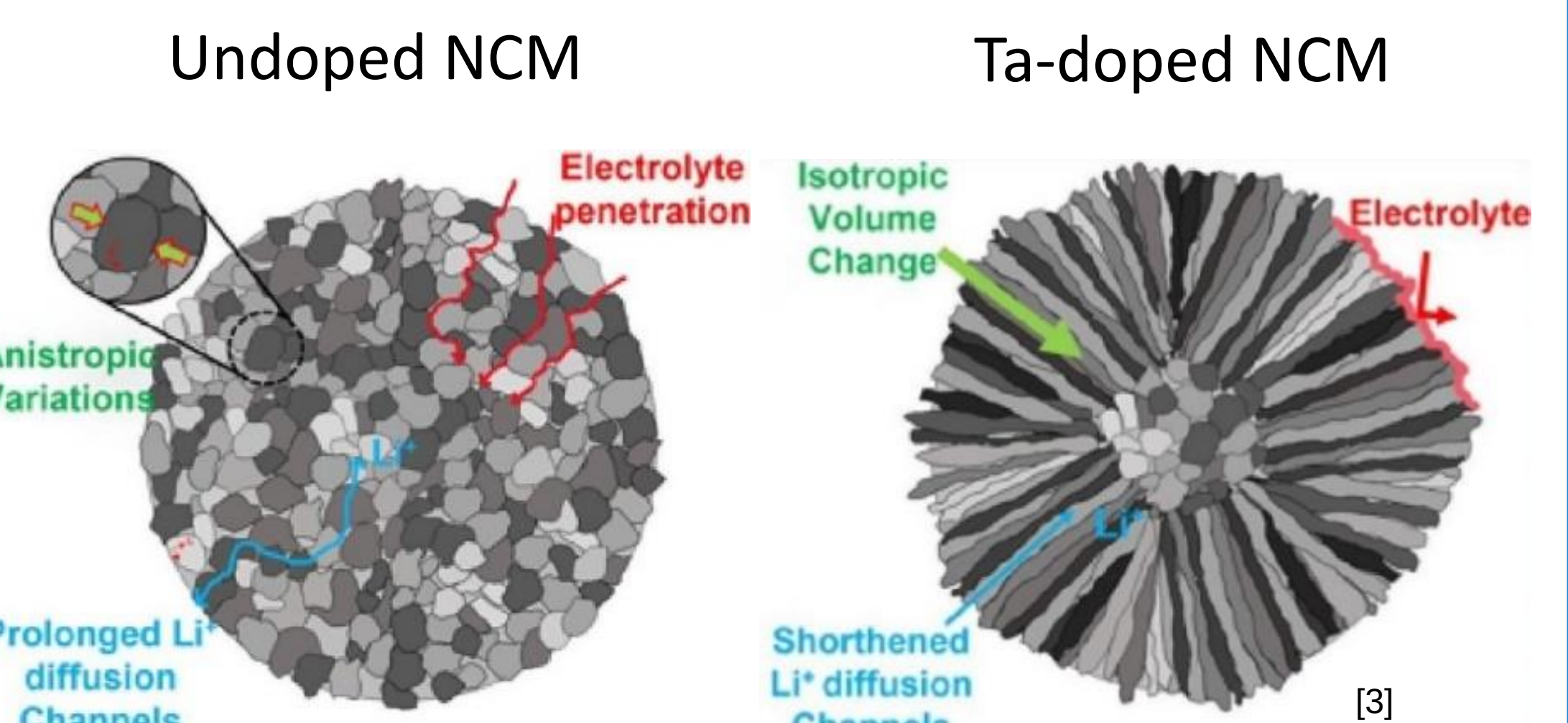
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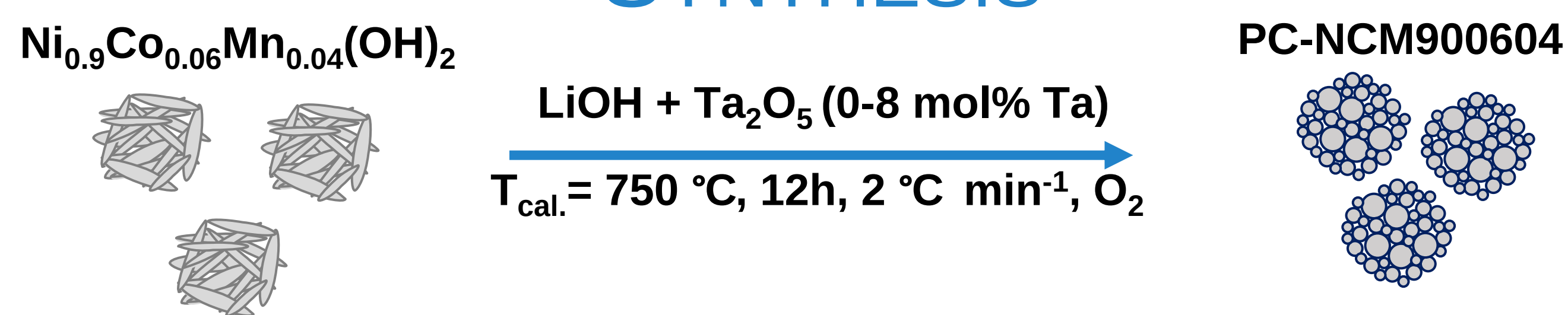
INTRODUCTION

The secondary agglomerated particles of state-of-the-art polycrystalline (PC) Ni-rich layered oxide cathode materials such as $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ ($x + y + z = 1$, NCMxyz where $x \geq 0.8$), which are composed of agglomerated primary particles, exhibit severe particle cracking due to the random orientation and their anisotropic volume changes. This anisotropic volume change forms stress at the grain boundaries of the primary particles inducing intergranular particle cracking. This promotes surface degradation mechanisms such as transition metal dissolution, inactive phase formation and electrolyte decomposition by continuously exposing fresh surface area during cycling. For Ni-rich PC-NCM, particle cracking is particularly detrimental to material stability and cycle life and this effect becomes more pronounced as the Ni content increases.^[1,2]

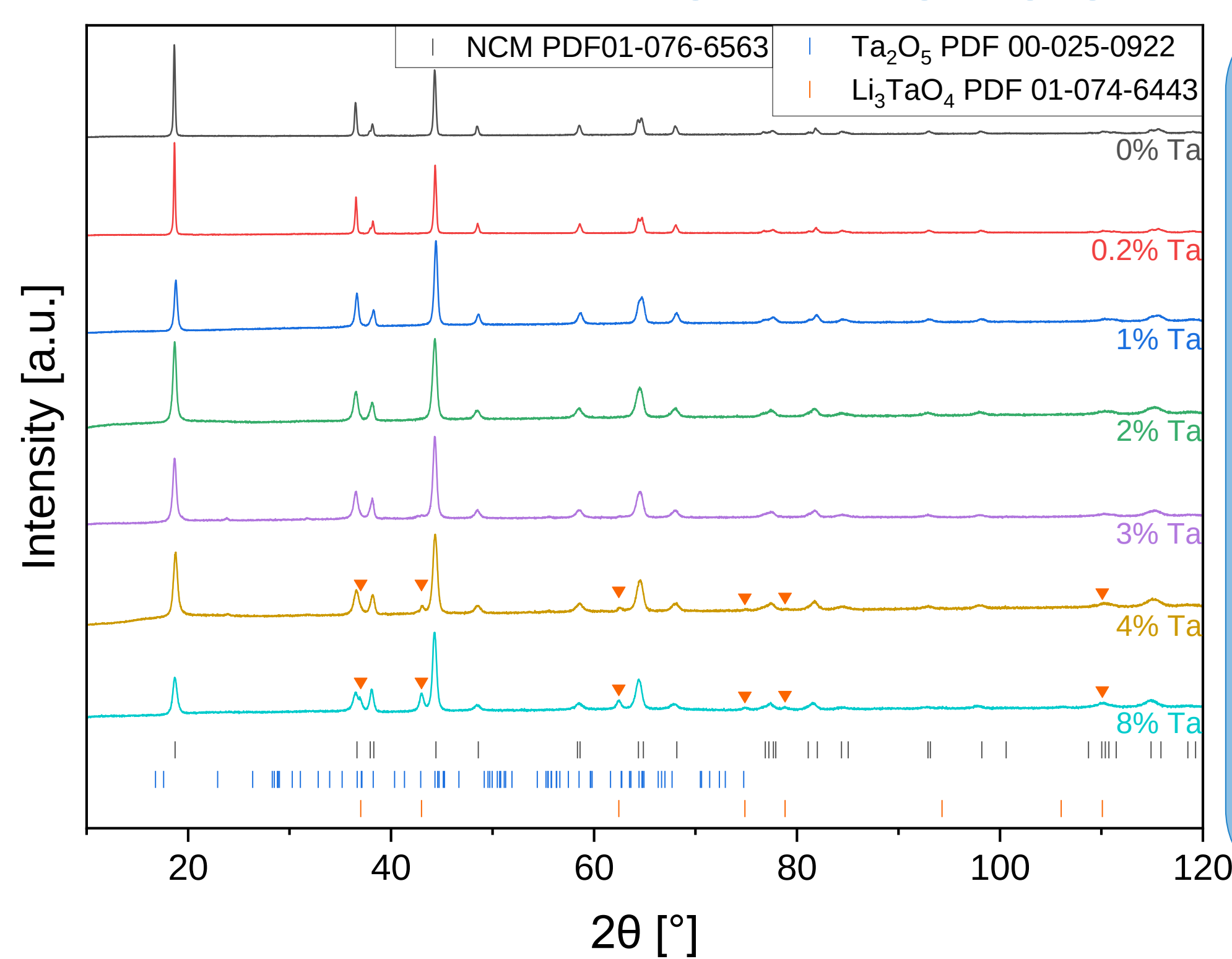
The use of Ta as dopant for PC-NCM can inhibit these parasitic reactions by changing the primary particle morphology. Instead of randomly ordered primary particles, rod-like particles are formed, which are aligned around the secondary particle core. This reduces the stress induced by anisotropic volume change inhibiting particle cracking and therefore these parasitic side reactions. Furthermore, the elongated primary particles should increase the Li^+ -diffusion increasing the rate capability of the cathode active material.^[3,4]



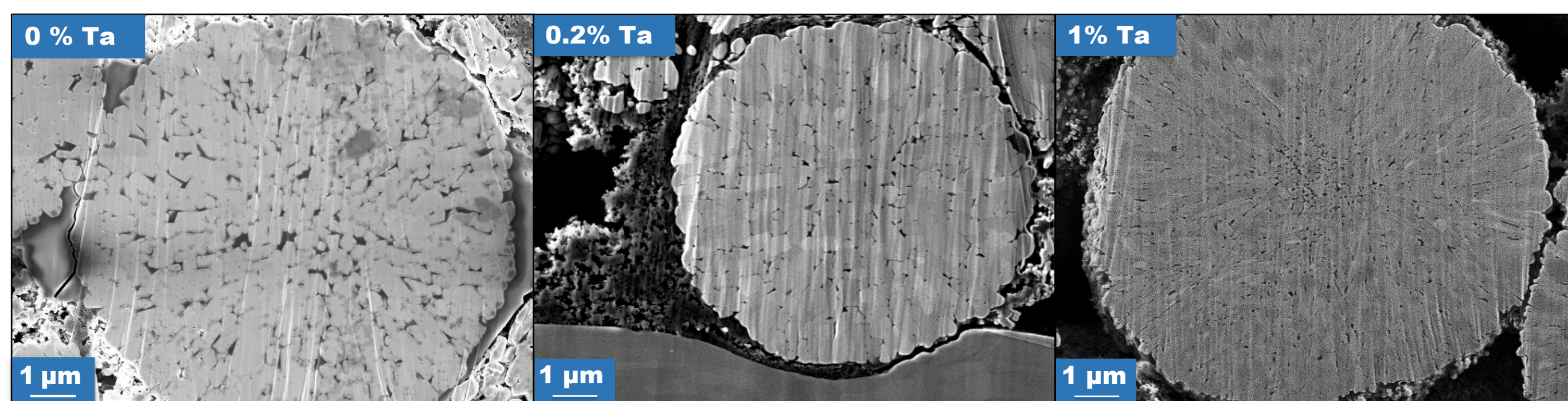
SYNTHESIS



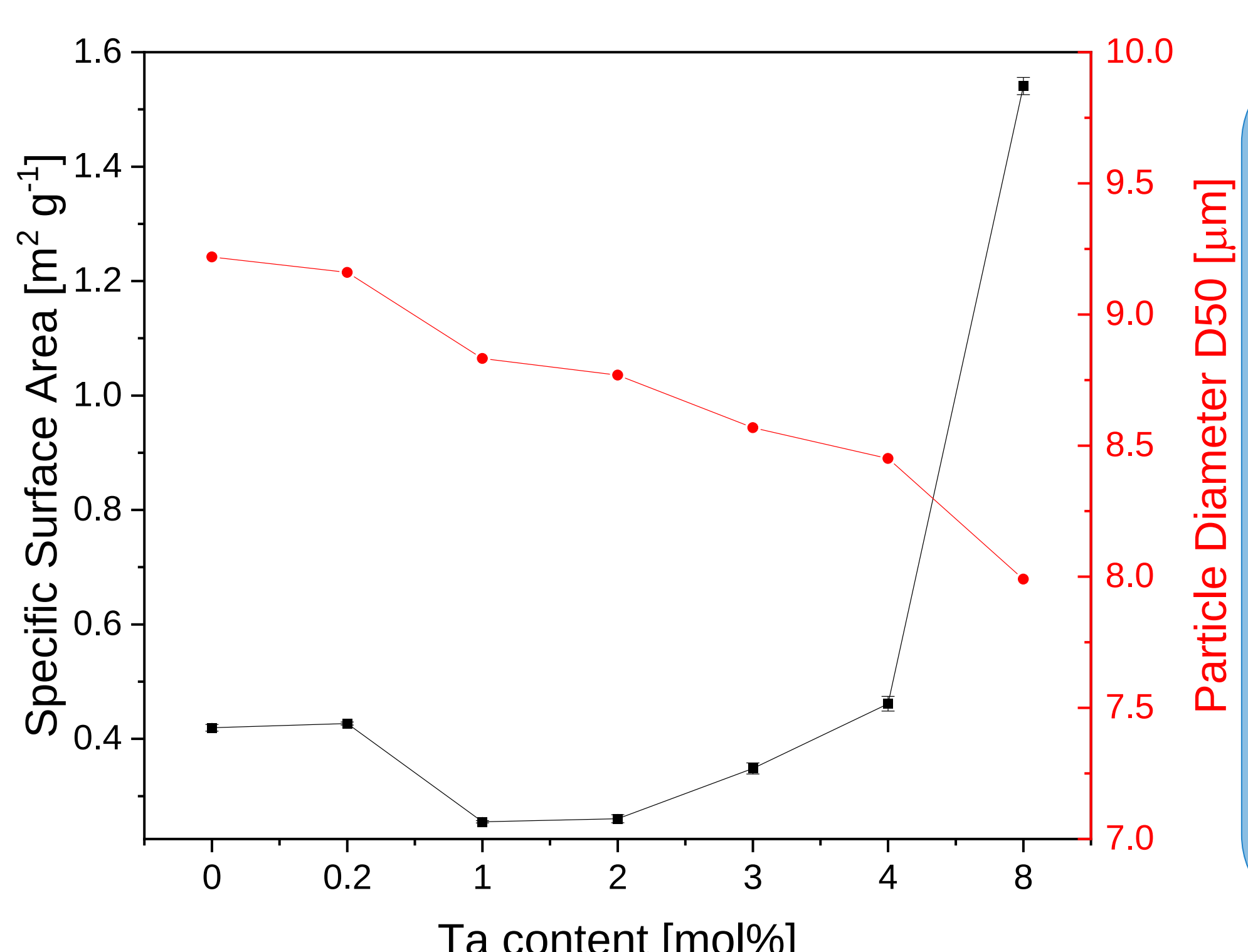
MORPHOLOGY



- Phase pure NCM for lower Ta amounts
- Appearance of a second phase with higher dopant amounts
- Formation of Li_3TaO_4
- No detectable Ta_2O_3 phase

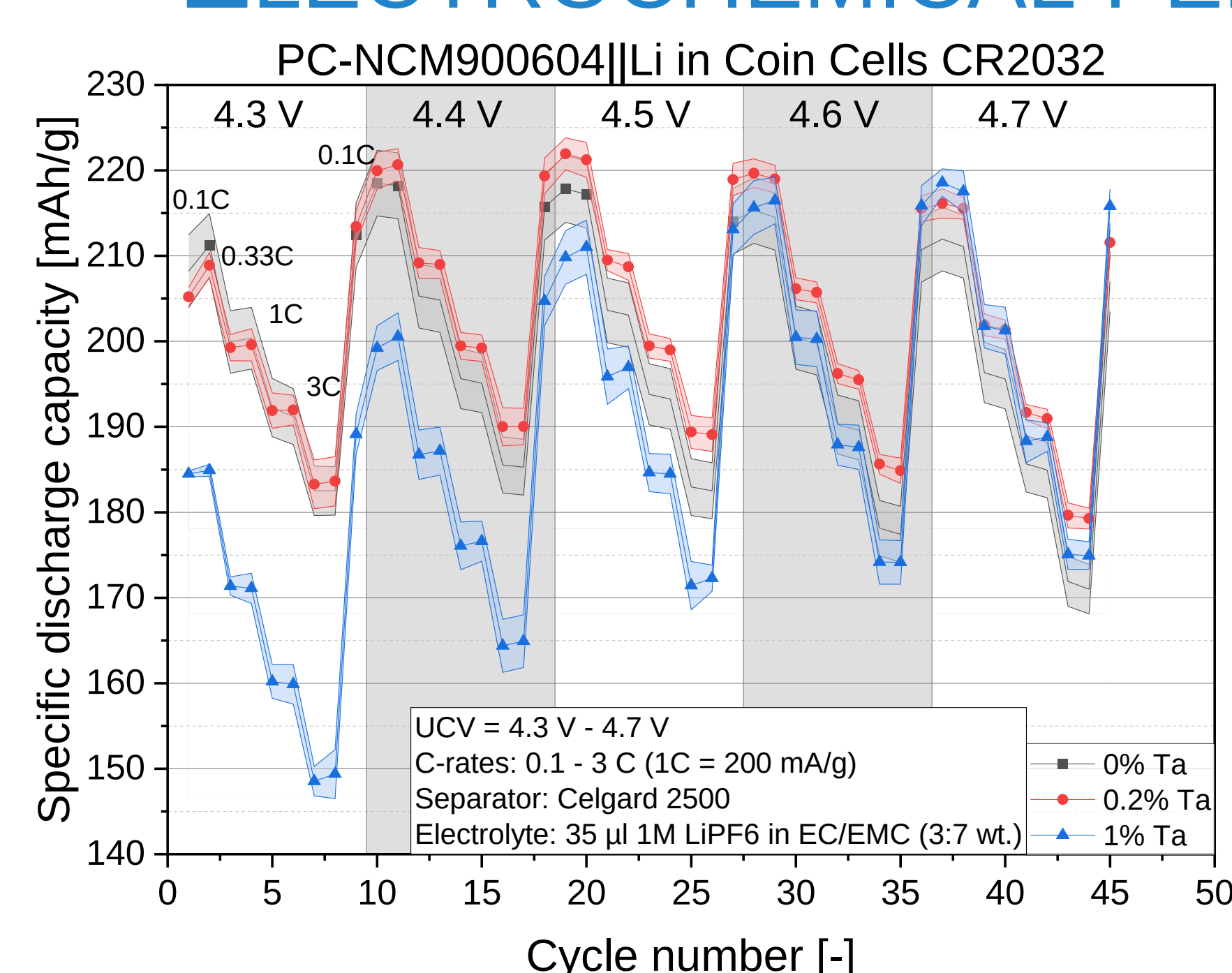


Change of primary particle shape and arrangement with increased Ta content
→ Elongation and radial alignment around the secondary particle core

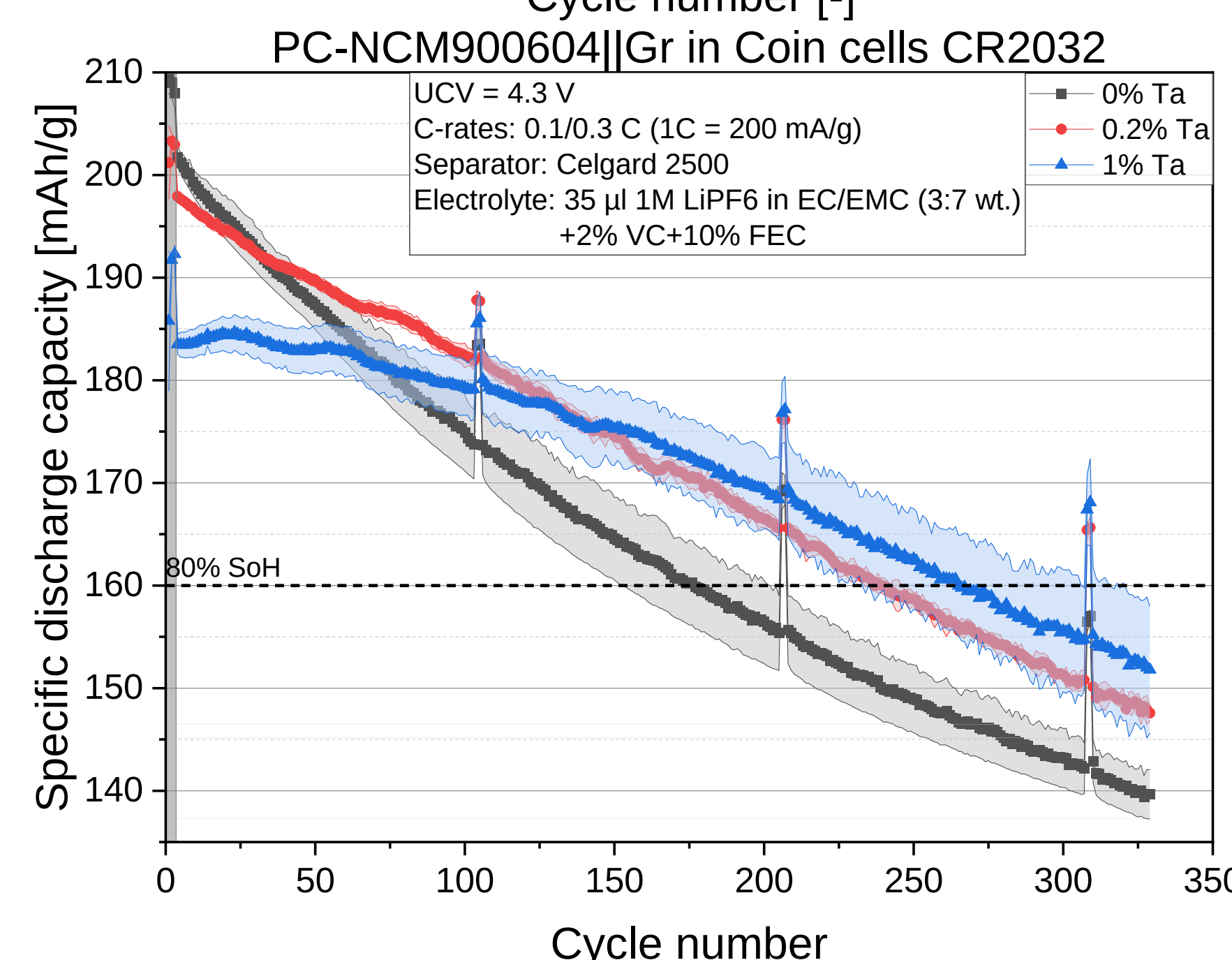


- Decreasing particle size with increasing Ta doping
- Decreasing specific surface area for low Ta amounts, but increasing for contents >2 mol% due to Li_3TaO_4 formed as a second phase

ELECTROCHEMICAL PERFORMANCE



- Initial capacity decreased with Ta-doping, especially at higher contents
- Ta improves capacity and C-rate performance at higher upper cut off voltages (UCV)



- Ta-doping decreases capacity, but improves cycle life
- 0.2 mol% shows most promising cycling behavior with similar capacity as without Ta and improved cycle life

CONCLUSIONS

- Li_3TaO_4 formed as second phase at higher Ta content (at ~3-4 mol% Ta)
- Ta-doping leads to change in primary particle microstructure from random to rod-like, radially aligned primary particles
- Particle size decreasing with Ta-doping
- Specific surface area decreasing for lower Ta content, but increasing at higher Ta content due to second phase formation
- Initial capacity decreasing with Ta amount, however at higher UCV Ta-doping seems beneficial
- 0.2 mol% Ta shows improved cycle life with similar capacity at 0.3C

ACKNOWLEDGMENTS

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