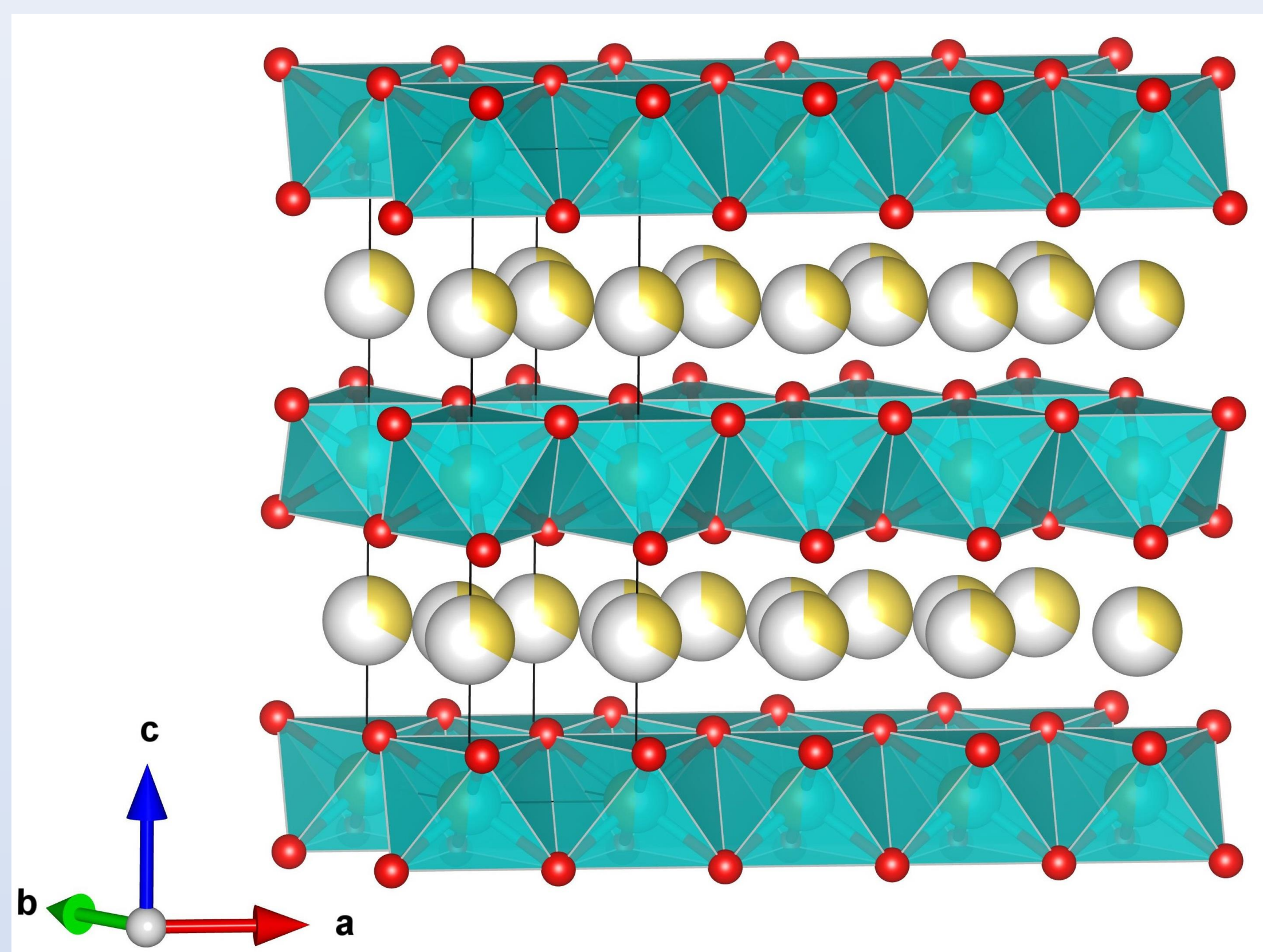


The role of surface coating in $\text{Na}_{0.67}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$: enhancing capacity and stability of cathodes for Sodium-Ion Batteries

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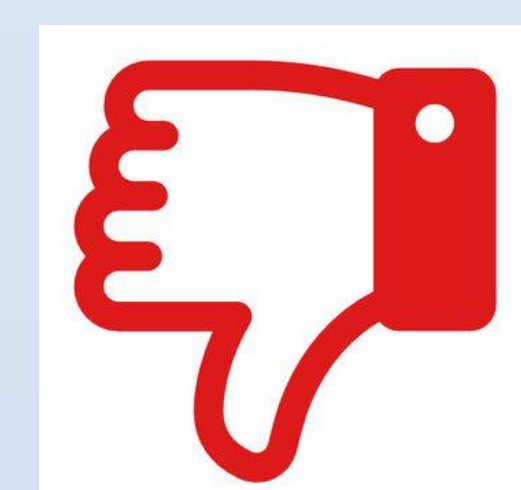
1. INTRODUCTION

Transition metal layered oxides, of general formula Na_xTmO_2 , are one of the most promising category of cathodic materials for Sodium-Ion Batteries (SIBs), due to their fast and highly reversible intercalation/deintercalation process, their facile synthesis and their good operating voltage.

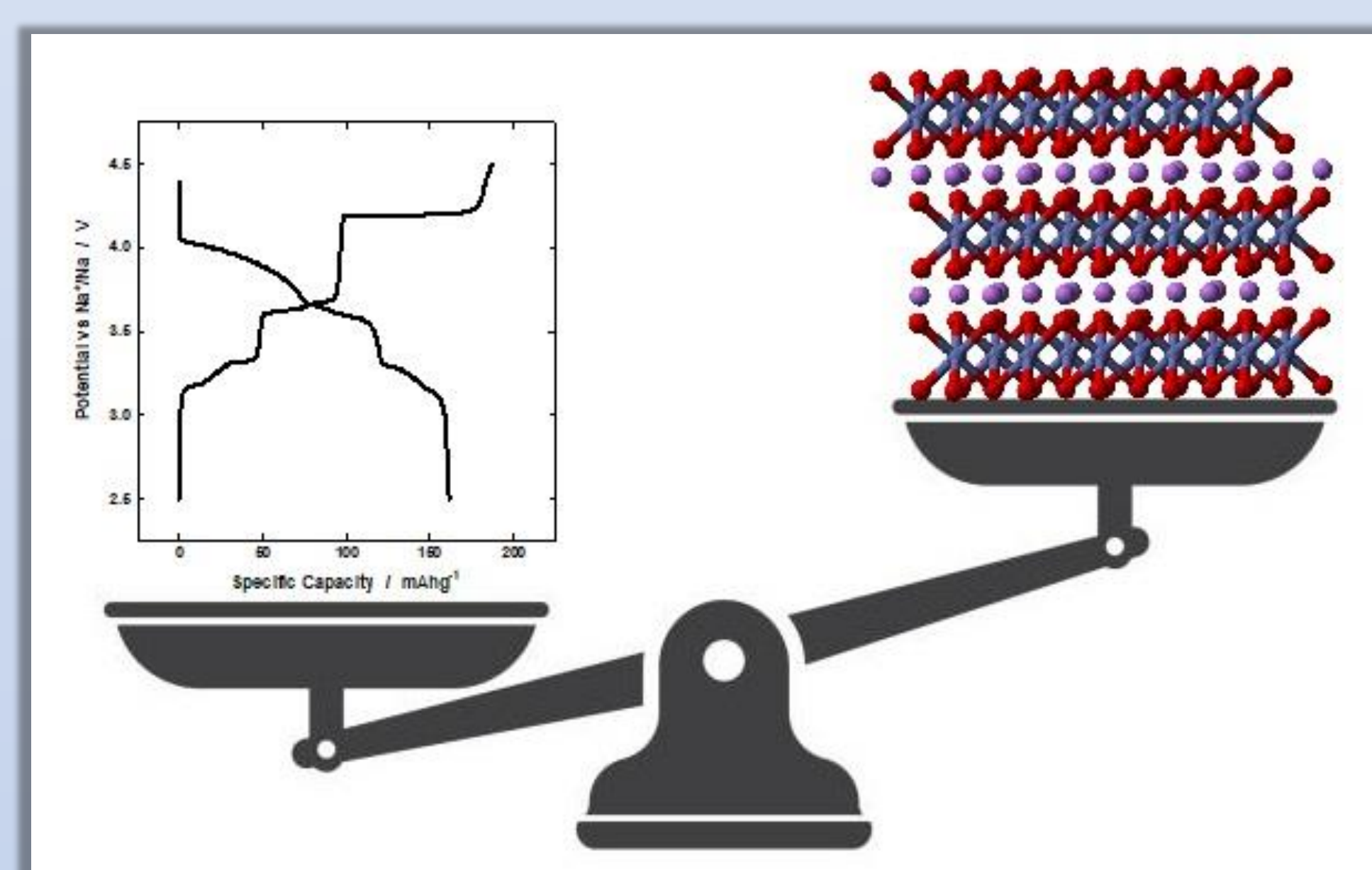
Many different materials with different compositions or different transition metals have been studied, among them one of the most promising is $\text{P2-Na}_{0.67}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$.



- Low cost
- Low Nickel content
- High operating voltage
- High stability between 2.5 and 4.1V vs Na^+/Na

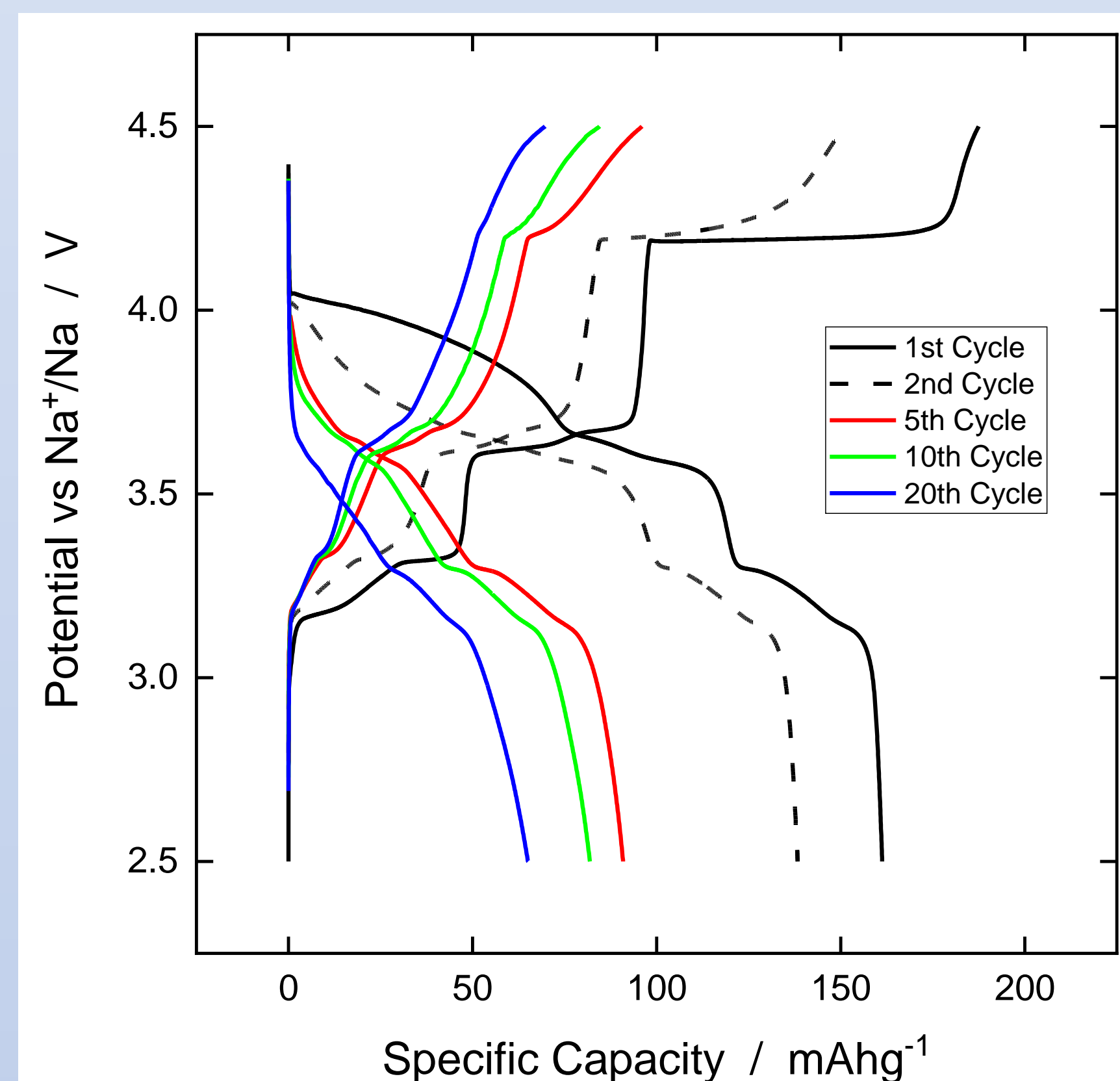


- Decomposes in water
- Very low stability between 2.5 and 4.5V vs Na^+/Na

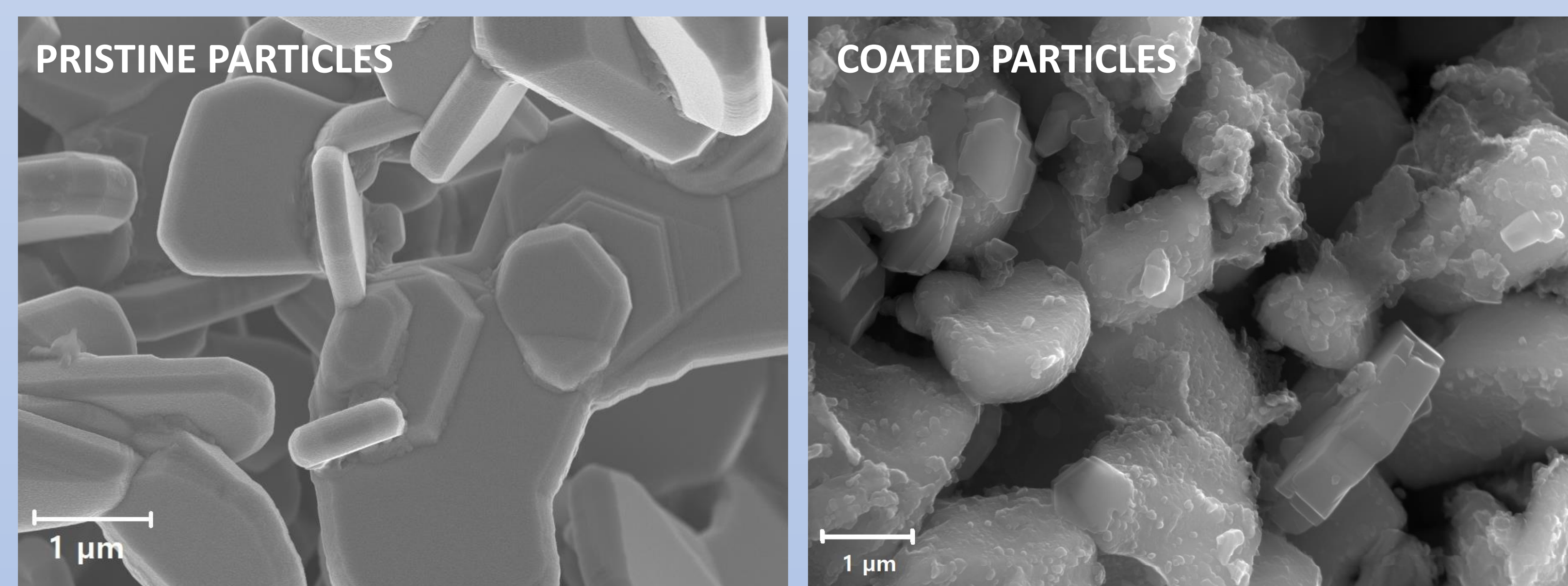


$\text{P2-Na}_{0.67}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$, when tested between 2.5 and 4.1V vs Na^+/Na , exhibits a specific capacity of $\approx 85\text{mAhg}^{-1}$, with a capacity retention upon cycling near 100%. That capacity is given by the contribution of two plateau, one at around 3.3V and one around 3.6V.

To obtain a better specific capacity and to increase the average operating voltage it's possible to test the material up to 4.5V vs Na^+/Na . In this case the capacity is significantly enhanced, but the capacity retention is extremely low.



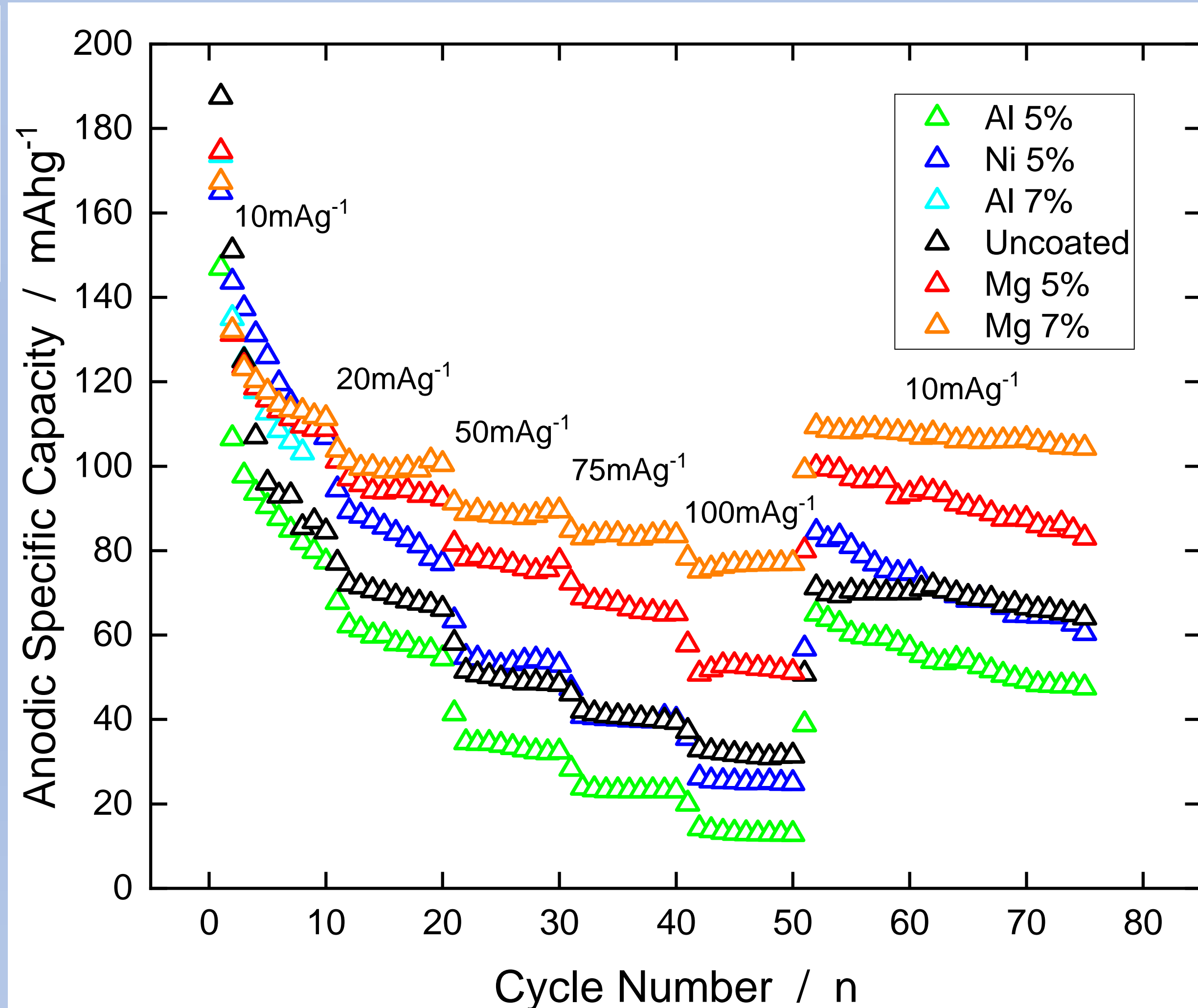
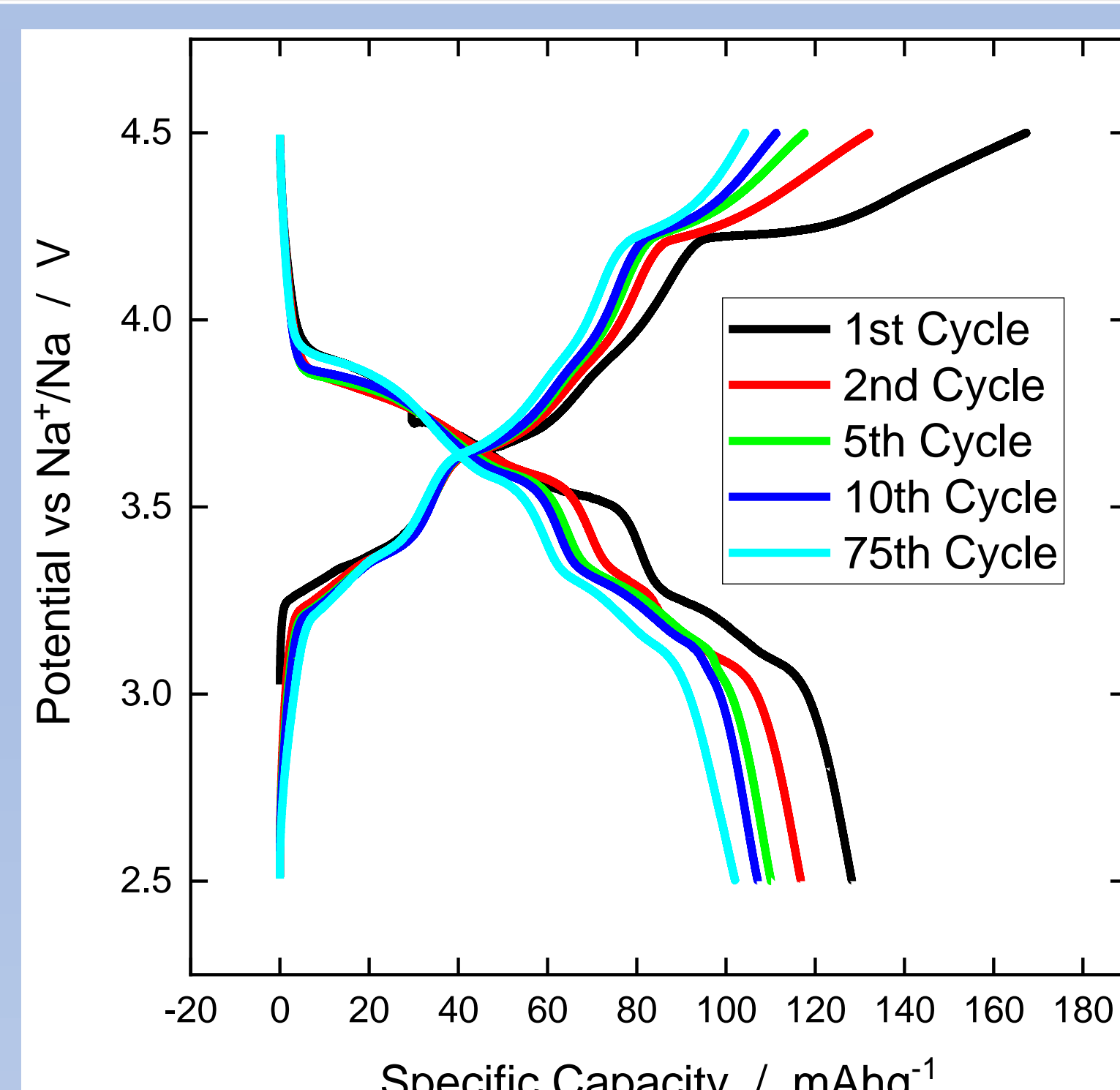
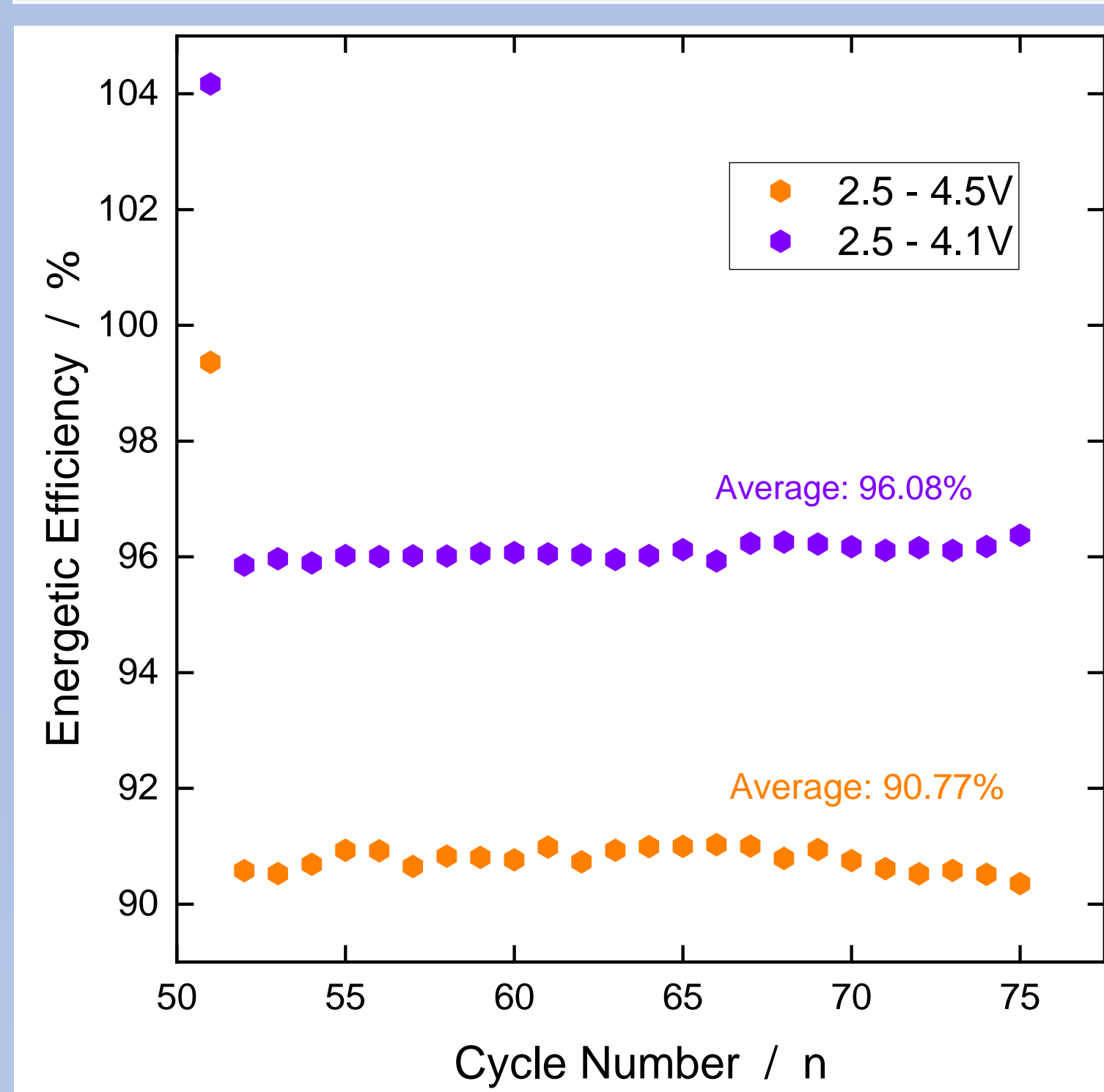
The fading of the material's performances is caused by **anionic redox reactions**. The plateau at 4.2V is originated by a $\text{O}^{2-}/\text{O}_2^{n-}/\text{O}_2$ process that leads to a surface densification of the cathodic particles, preventing the intercalation/deintercalation process^[1].



One approach to solve the problem of the material's irreversibility is to performed an inorganic coating on the cathodic particles^[2,3].

In particular we coated the active material's powders with four different metal oxides (MgO , NiO , Al_2O_3 , ZrO_2) in four different mass percentages (3, 5, 7%). All the materials were obtained as pure phase, unless the ZrO coated ones, where the oxide was present as a secondary phase.

The coated materials, especially the ones coated MgO , showed a clear improvement in the electrochemical performances. The MgO 7% coated sample showed a quasi-stable capacity of almost 110mAhg^{-1} at a current value of 10mAhg^{-1} , confirming that this treatment can be an effective way to enhance the layered oxides specific capacity.



Actually, the MgO 7% coated sample is being studied by means of Electrochemical Impedance Spectroscopy and X-Ray Photoelectron Spectroscopy, to better understand the durability and the effects of the coating.

Future perspective will be about trying more homogeneous coating on the active material's particles, for example with Atomic Layer Deposition.

[1]Zhang et al., ACS Cent. Sci. 2020, 6, 232–240

[2] Liu et al., Nano Energy 2016, 27, 27-34

[3] Li et al., Electrochim. Acta, 2006, 51, 3872-3883