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Thermal stability of $\text{Na}_{3-x}\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$: influence of F^- for O^{2-} substitution and degradation mechanism

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$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) is currently considered as one of the more efficient positive electrode material for practical use in Na-ion batteries.¹⁻³ Its attractive theoretical capacity of 128 mAh/g, obtained by the reversible extraction of two Na^+ ions per formula unit at an average potential of 3.95 V vs Na^+/Na , leads to theoretical energy density of ~500 Wh/kg, which is comparable to that delivered by LiFePO_4 in Li-ion batteries. Since the first report of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ as positive electrode material in full cells vs hard carbon in 2013,⁴ a lot of research is still done to optimize NVPF rate capability by tailoring particle morphology or conductive coatings. Nevertheless, few has been reported on its thermal stability upon cycling, despite crucial for practical applications. Indeed, the degradation mechanisms need to be investigated at different states of charge, to understand the possible reactions happening during a thermal runaway.

A series of carbon-coated $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($y = 0, 0.07$ and 0.12) materials were synthesized to investigate the impact of a low oxygen for fluorine substitution on the thermal stability of $\text{NVPF}_{\text{O}_y}/\text{C}$ at different states of charge or discharged, and to understand the thermal degradation mechanisms in contact with electrolyte. Globally, the O^{2-} for F^- substitution has a very limited effect on the thermal stability of fully discharged materials, whereas it has a beneficial impact for charged ones (**Fig. 1**). Indeed, the thermal degradation occurs at slightly higher temperature with less intense exothermic reaction for partially and fully charged electrode materials. Moreover, whatever the state of charge and the oxygen content in $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($1 \leq x \leq 3$ and $y = 0, 0.07$ and 0.12), the thermal degradation leads, quite surprisingly, to the formation of crystalline $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ in addition to an amorphous phase (**Fig. 1**).⁵ This reaction is similar with or without presence of electrolyte salt. The fluorination of the partially

oxygen for fluorine substituted material was clearly demonstrated by XRD and NMR on post DSC materials. Further investigations are currently done to understand more in detail the role of PVDF binder in the fluorination process and the vanadium reduction upon Na^+ re-intercalation.

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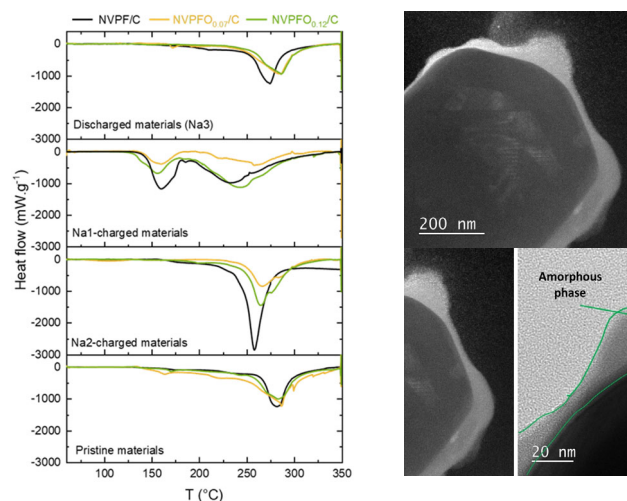


Figure 1: (left) DSC curves of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{C}$ (black), $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.93}\text{O}_{0.07}/\text{C}$ (yellow) and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.88}\text{O}_{0.12}/\text{C}$ (green) at different states of charge or discharge. (right) TEM images of Na1-charged NVPF/C recovered after DSC experiment.