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Solid state NMR characterization of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ positive electrode materials for Na-ion batteries

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In the scope of finding new positive electrode materials for Li-ion and Na-ion batteries, the deep understanding of the link between their structure, electronic structure and electrochemical behavior is crucial. To that extent, Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) appeared to be a key tool, as for paramagnetic materials, it allows to probe both, the local structure and the local electronic structure thanks to the hyperfine interaction.

Using ^{23}Na and ^{31}P MAS-NMR we studied the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ series, which are promising materials for positive electrode application Na-ion batteries. We showed that the end member $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ exhibits some O-defects leading to the formation of V^{4+} ions locally. NMR combined with DFT calculations, allows to characterize the very specific electronic configuration around V^{4+} ions forming a vanadyl-type bond with the O-defect, that affects the electrochemical cycling performances.

Na^+ ions deintercalation mechanism was also investigated by ^{23}Na and ^{31}P MAS NMR for two different systems: $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_2\text{O}$. Finally we investigated the thermal stability of a series of $\text{Na}_x\text{V}^{3+}_{2-y}\text{V}^{4+}_y(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($0 \leq y \leq 2$) materials in order to learn more about the influence of F^- for O^{2-} substitution and the state of charge. NMR studies were crucial to understand the degradation mechanisms.