

## Supporting Information

### Impact of the F<sup>-</sup> for O<sup>2-</sup> substitution in Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3-y</sub>O<sub>y</sub> on their transport properties and electrochemical performance

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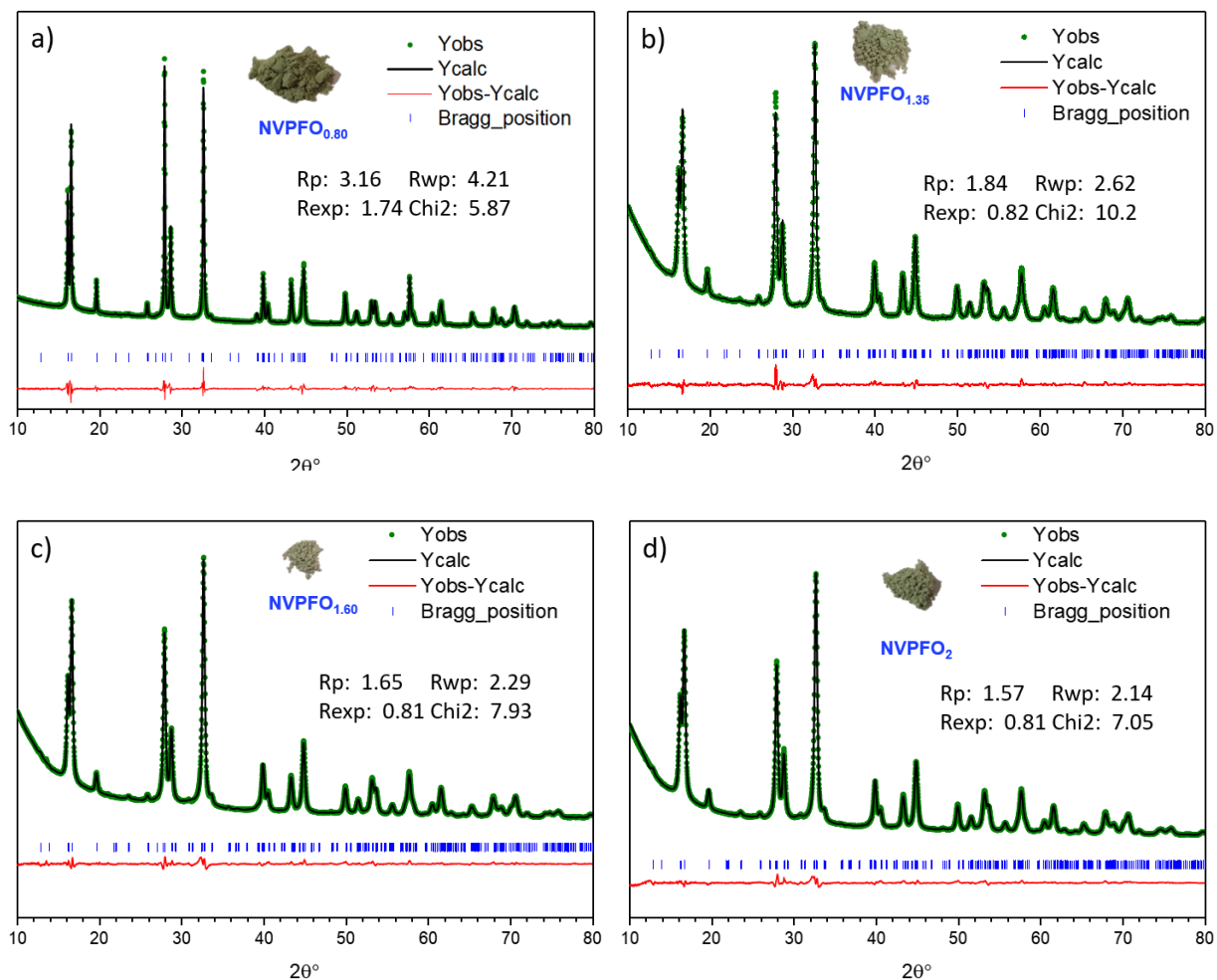


Figure S1. Rietveld refinement of the XRD data for the different compounds  $NVPFO_{0.80}$ ,  $NVPFO_{1.35}$ ,  $NVPFO_{1.60}$  and  $NVPFO_2$ .

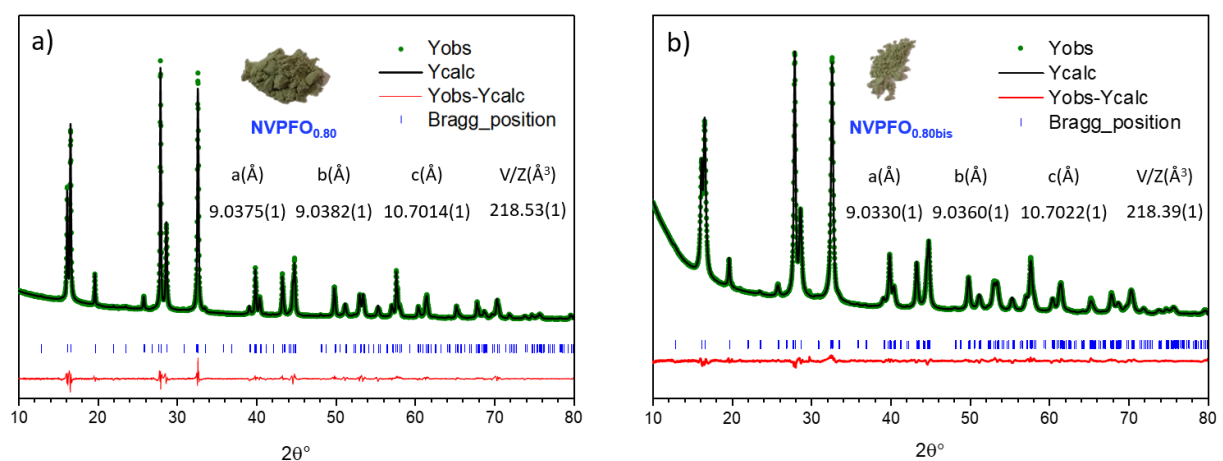


Figure S2. The cell parameter comparison of the  $NVPFO_{0.80}$  and  $NVPFO_{0.80bis}$

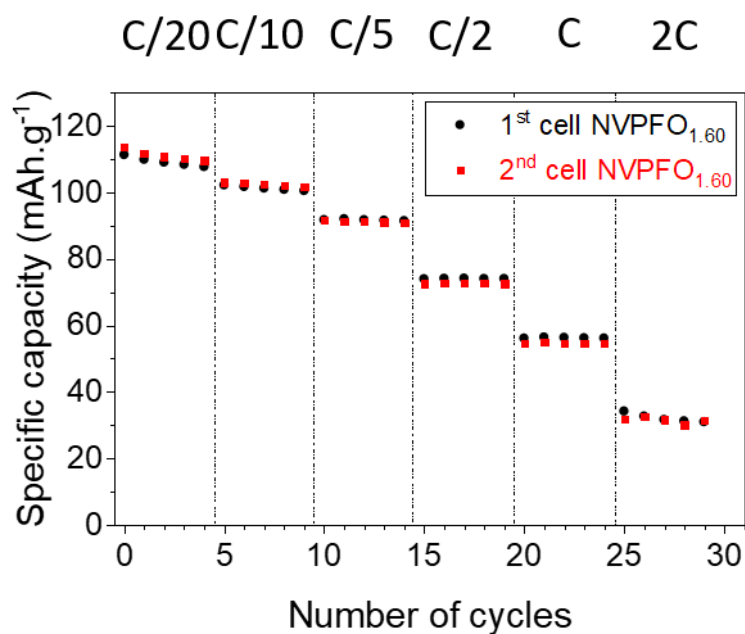


Figure S3. Illustration of the reproducibility of the electrochemical performance obtained for NVPFO<sub>1.6</sub>.

This shows an example of the reproducibility of the electrochemical tests that were performed for NVPFO<sub>1.6</sub>. The reproducibility tests validate that the different performance in the study are induced by the different chemical composition and not influenced by the experimental cell assembly.

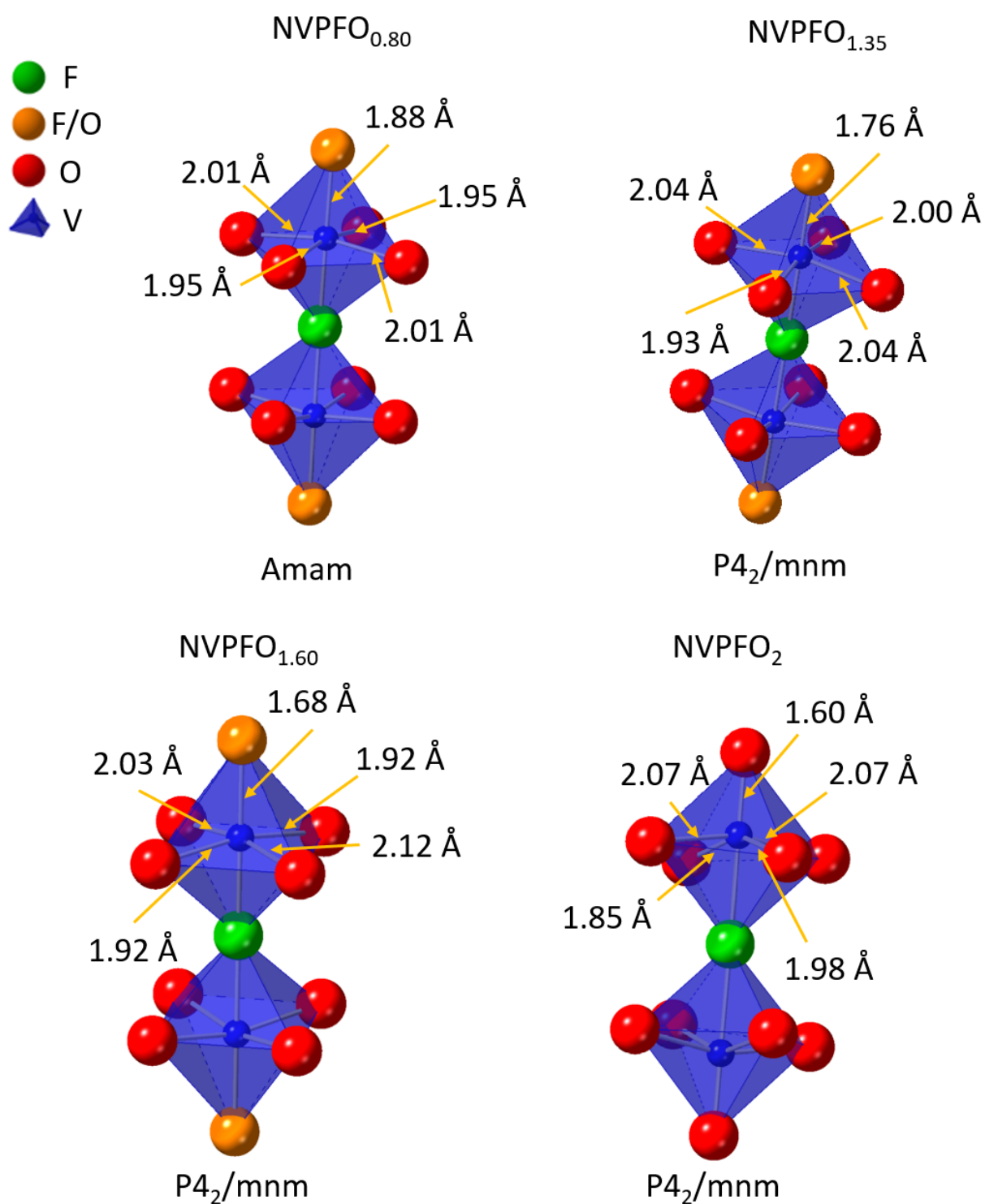


Figure S4. Illustration of bond distance changes from the composition NVPFO<sub>0.80</sub> to the composition NVPFO<sub>2</sub>.

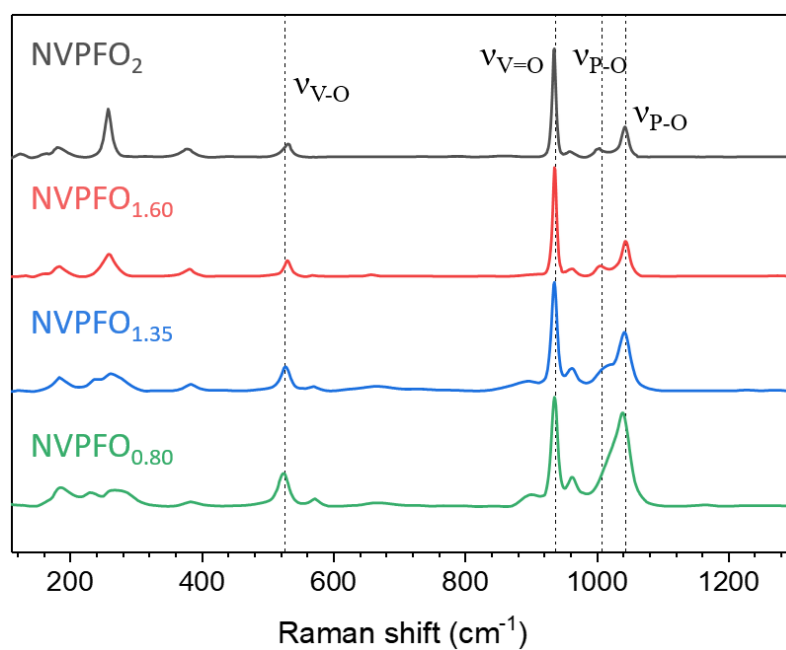


Figure S5. All Raman spectra from 100  $\text{cm}^{-1}$  to 1300  $\text{cm}^{-1}$ . The spectra were corrected to remove the background. The absence of signal after 1150  $\text{cm}^{-1}$  confirmed the absence of carbon in the compounds (absence of D-band, see Figure S6)<sup>1</sup>.

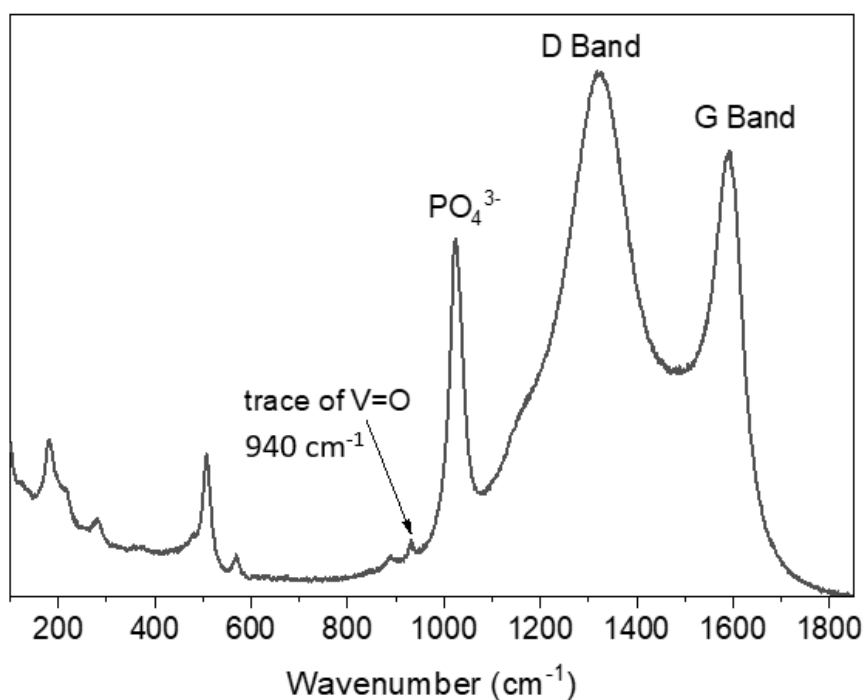


Figure S6. Raman spectrum of carbon-coated  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  ( $y=0$ ). The electrode material was synthesized through the method proposed by Hall et al.<sup>2</sup> This spectrum confirms the absence of carbon in the series studied in this work (absence of signal around  $1150\text{--}1300\text{ cm}^{-1}$  as shown in Figure S5) and endorses the attribution of the signal at  $940\text{ cm}^{-1}$  to vanadyl bond vibration since this signal nearly disappears for  $\text{Na}_3\text{V}^{3+}_2(\text{PO}_4)_2\text{F}_3$ . Indeed, as reported previously, a small amount of vanadyl type defects is always identified, which explains the detection of the signal at  $940\text{ cm}^{-1}$ .<sup>3</sup>

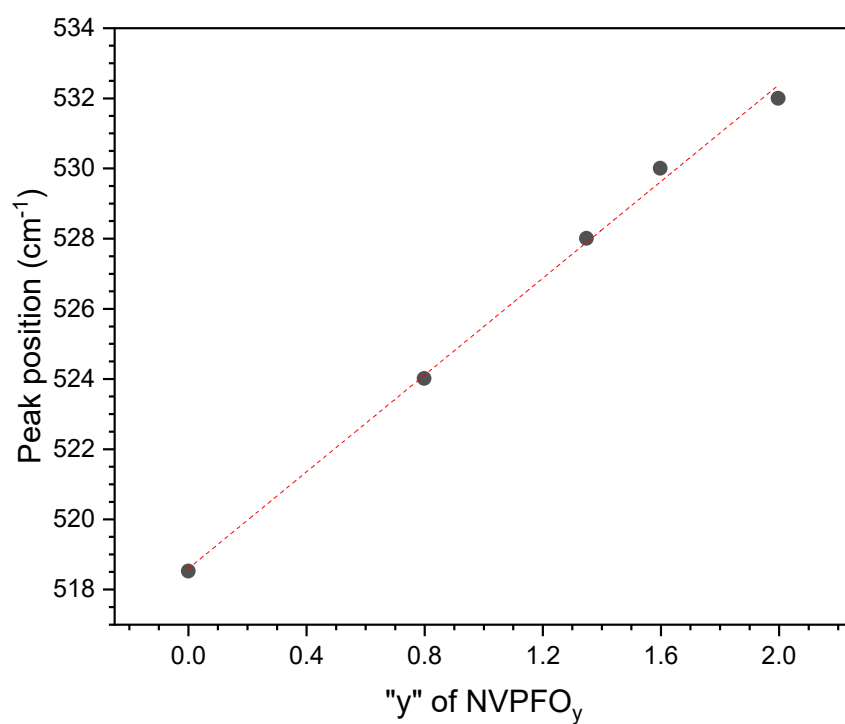


Figure S7. "y" of NVPFO<sub>y</sub> variation versus the shift of the V-O peak position. The linear fitting in red clearly demonstrates a linear shift of the peak according to the chemical formulae. The position of V-O band for NVPF3 (y=0) is measured from the spectrum reported in figure S6.

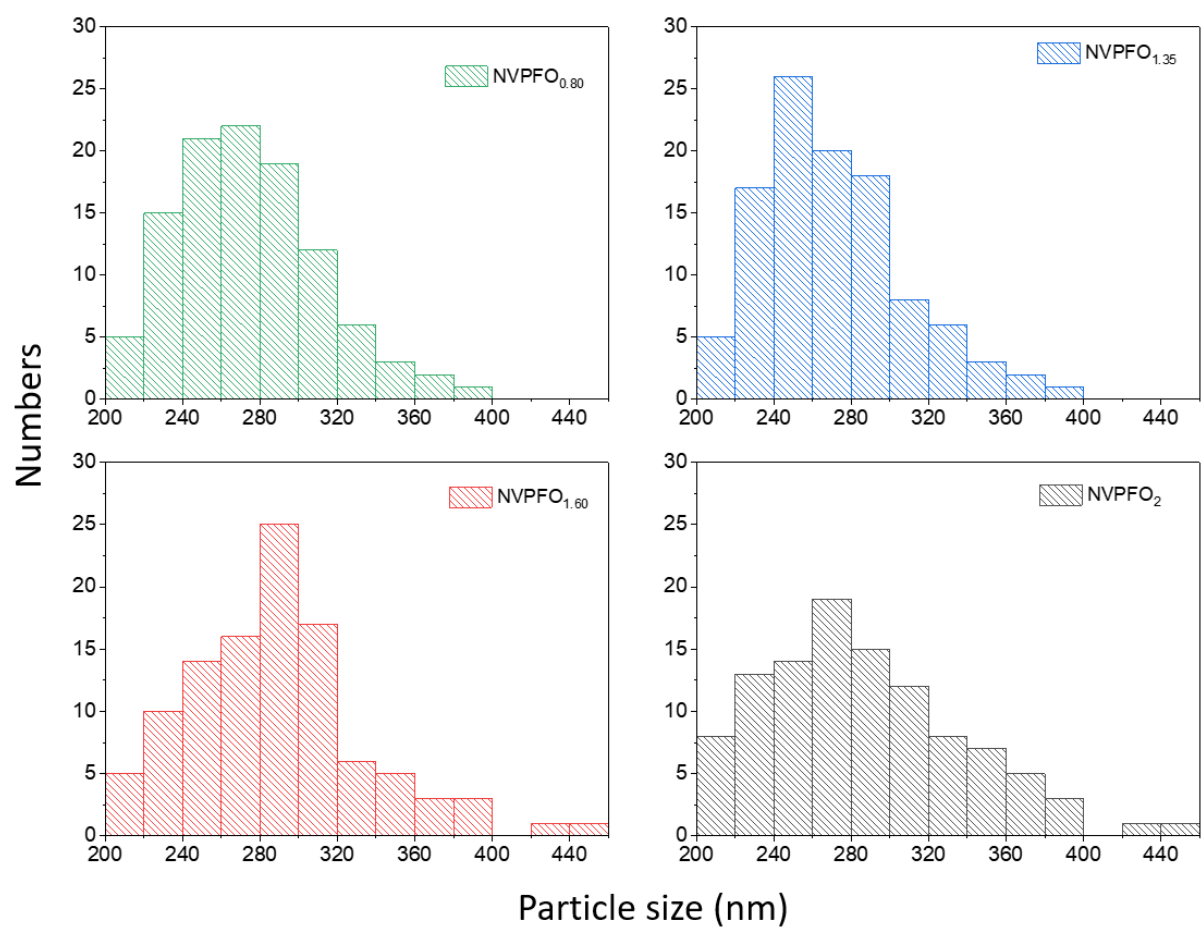


Figure S8. Statistics of particle size distribution for all the materials. For each material 106 particles were measured.



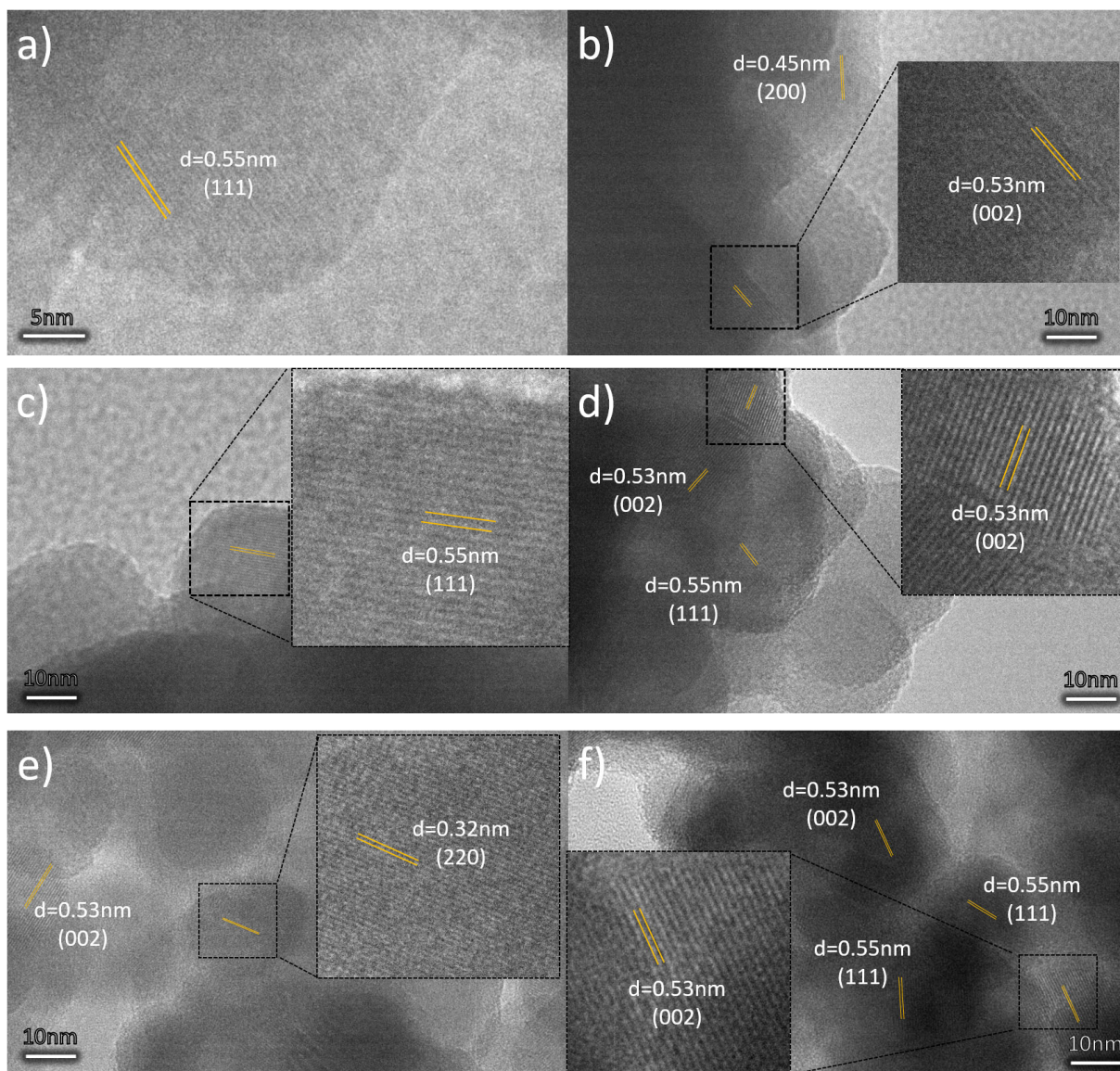


Figure S9. HRTEM images of a-b) NVPFO<sub>0.80</sub>, c-d) NVPFO<sub>1.60</sub> and e-f) NVPFO<sub>2</sub>.

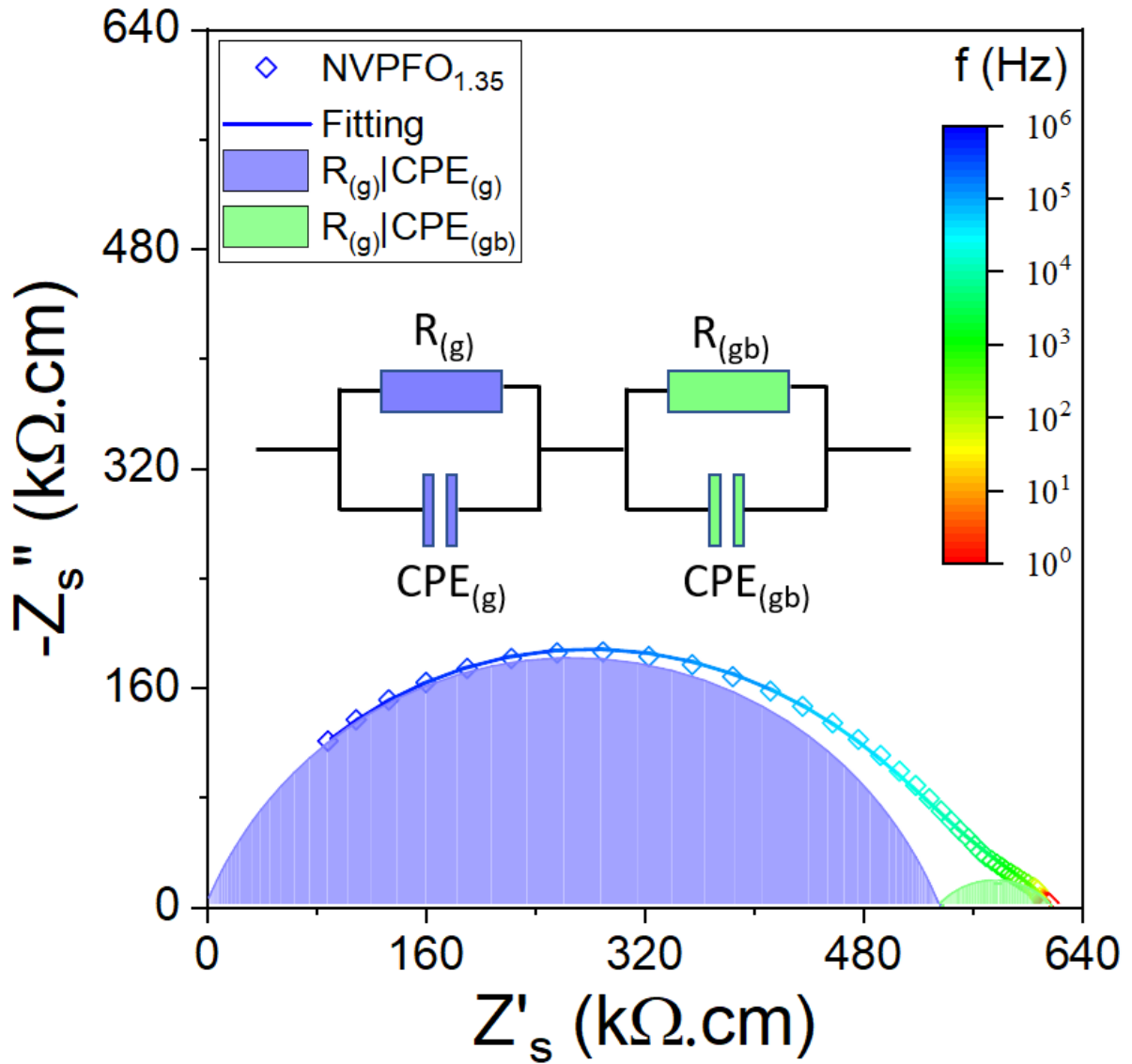


Figure S10. Deconvolution of grain and grain boundary contributions of complex impedance data recorded at  $200\text{ }^{\circ}\text{C}$  for  $\text{NVPFO}_{1.35}$  sample. The complex impedance data shown here have already been normalized regarding the shape factor of the sample. The shown equivalent circuit is used for impedance data fitting. Acronyms  $R$  and  $\text{CPE}$  represent resistive and constant phase elements whereas  $g$  and  $gb$  stand for grain and grain boundary contributions, respectively. The obtained effective specific capacitances or the relative permittivities are typical from grain ( $1.4\text{ pF}\cdot\text{cm}^{-1}$  or 15) and grain boundary ( $470\text{ pF}\cdot\text{cm}^{-1}$  or  $5329^4$ ) contributions.

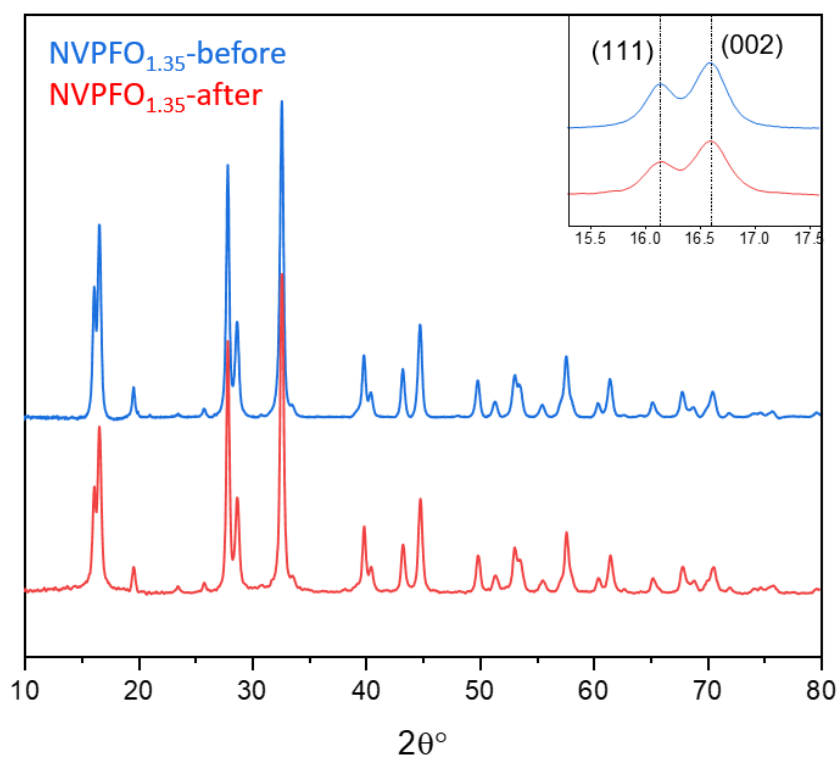


Figure S11. Comparison of the XRD patterns collected for  $\text{NVPFO}_{1.35}$ , before and after the impedance measurement, with inset of enlarged (111) and (002) peaks.

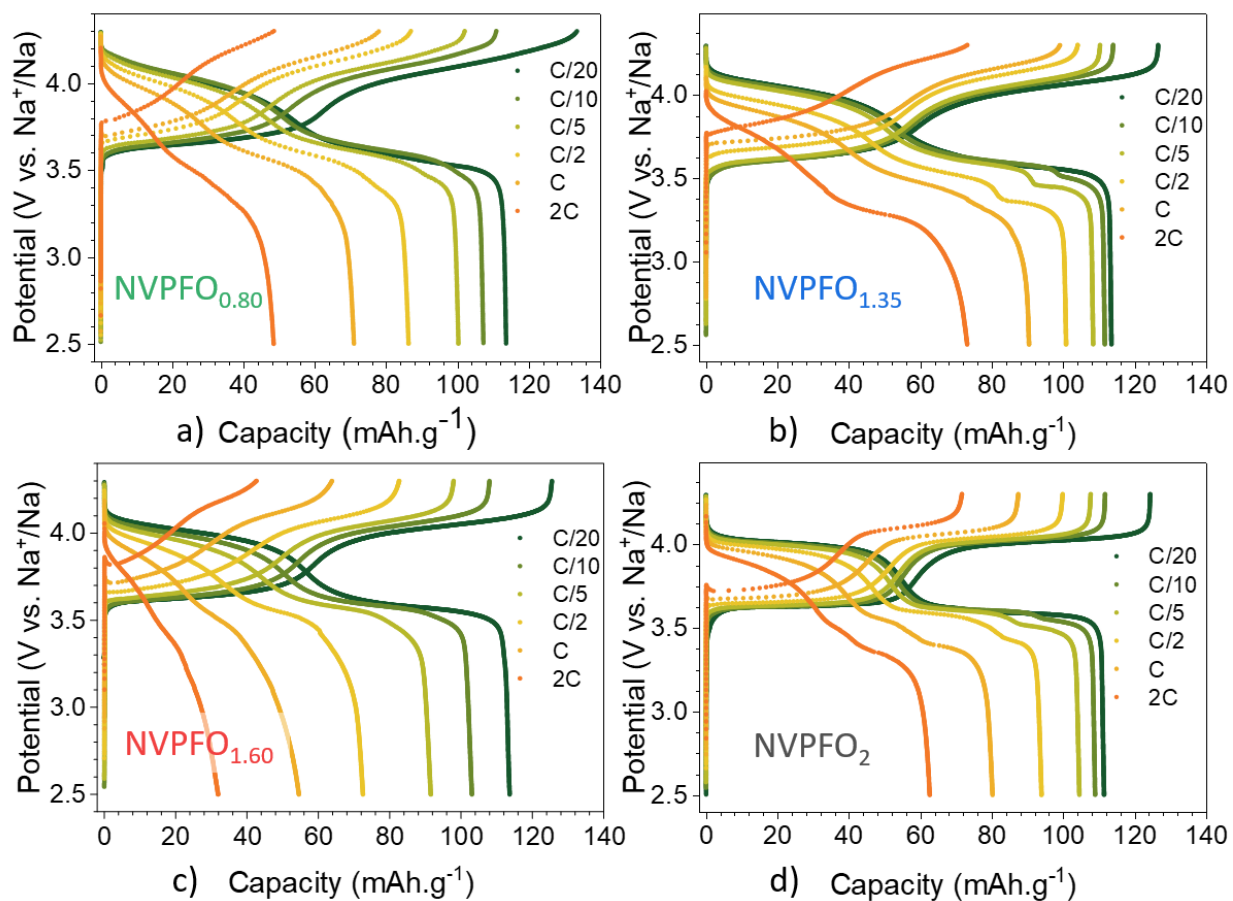


Figure S12. Charge and discharge curves of NVPFO<sub>y</sub> materials at different cycling rates, from C/20 to 2C.

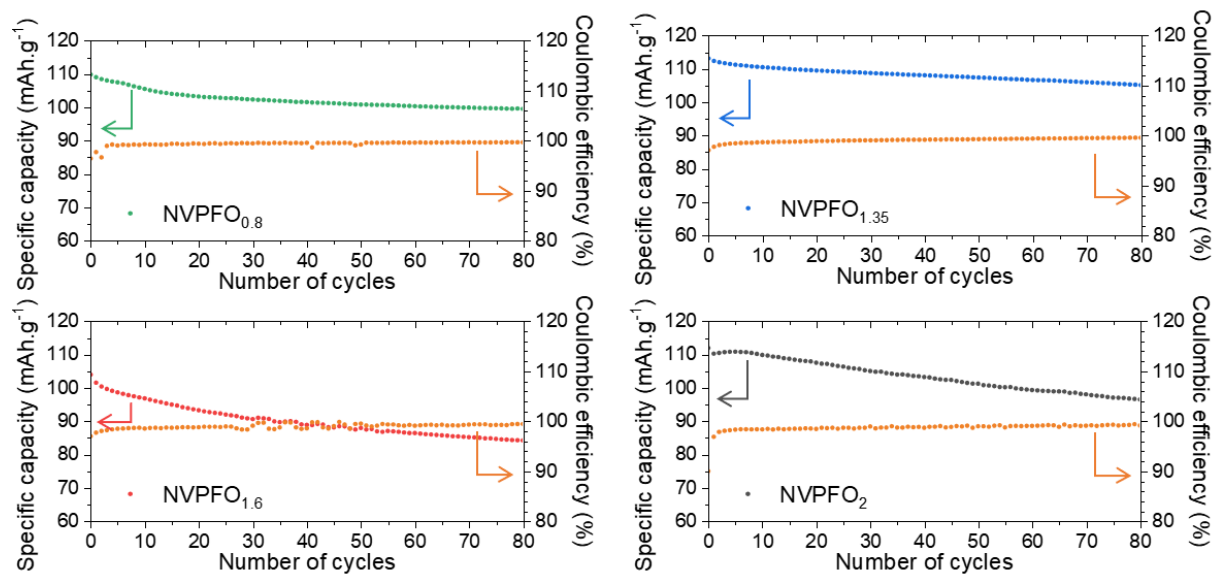


Figure S13. Long range cycling performance (specific capacity and Coulombic efficiency) at C/10 for NVPFO<sub>x</sub>.

## Bibliography:

- (1) Cai, Y.; Cao, X.; Luo, Z.; Fang, G.; Liu, F.; Zhou, J.; Pan, A.; Liang, S. Caging Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> Microcubes in Cross-Linked Graphene Enabling Ultrafast Sodium Storage and Long-Term Cycling. *Adv. Sci.* **2018**, 5 (9). <https://doi.org/10.1002/advs.201800680>.
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- (4) Irvine, J. T. S.; Sinclair, D. C.; West, A. R. Electroceramics: Characterization by Impedance Spectroscopy. *Adv. Mater.* **1990**, 2 (3), 132–138. <https://doi.org/10.1002/ADMA.19900020304>.