

Supporting Information

High Rate Performance for Carbon Coated Na₃V₂(PO₄)₂F₃ in Na-ion batteries

Thibault. Broux^{1,2,6,7}, *François Fauth*³, *Nikita Hall*⁴, *Yohann Chatillon*⁴, *Matteo Bianchini*^{1,2,5}, *Tahya Bamine*^{1,6}, *Jean-Bernard Leriche*², *Emmanuelle Suard*⁵, *Dany Carlier*^{1,6}, *Yvan Reynier*⁴, *Loïc Simonin*⁴, *Christian Masquelier*^{2,6,7} and *Laurence Croguennec*^{1,6,7,*}

¹ CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB UMR 5026, F-33600 Pessac, France.

² Laboratoire de Réactivité et de Chimie des Solides, CNRS-UMR#7314, Université de Picardie Jules Verne, F-80039 Amiens Cedex 1, France

³ CELLS - ALBA synchrotron, E-08290 Cerdanyola del Vallès, Barcelona, Spain

⁴ Univ. Grenoble Alpes, F-38000 Grenoble,

CEA, LITEN, 17 rue des Martyrs, F-38054 Grenoble cedex 9, France

⁵ Institut Laue-Langevin, 71 Avenue des Martyrs, F-38000 Grenoble, France

⁶ RS2E, Réseau Français sur le Stockage Electrochimique de l'Énergie, FR CNRS 3459, F-80039 Amiens Cedex 1, France

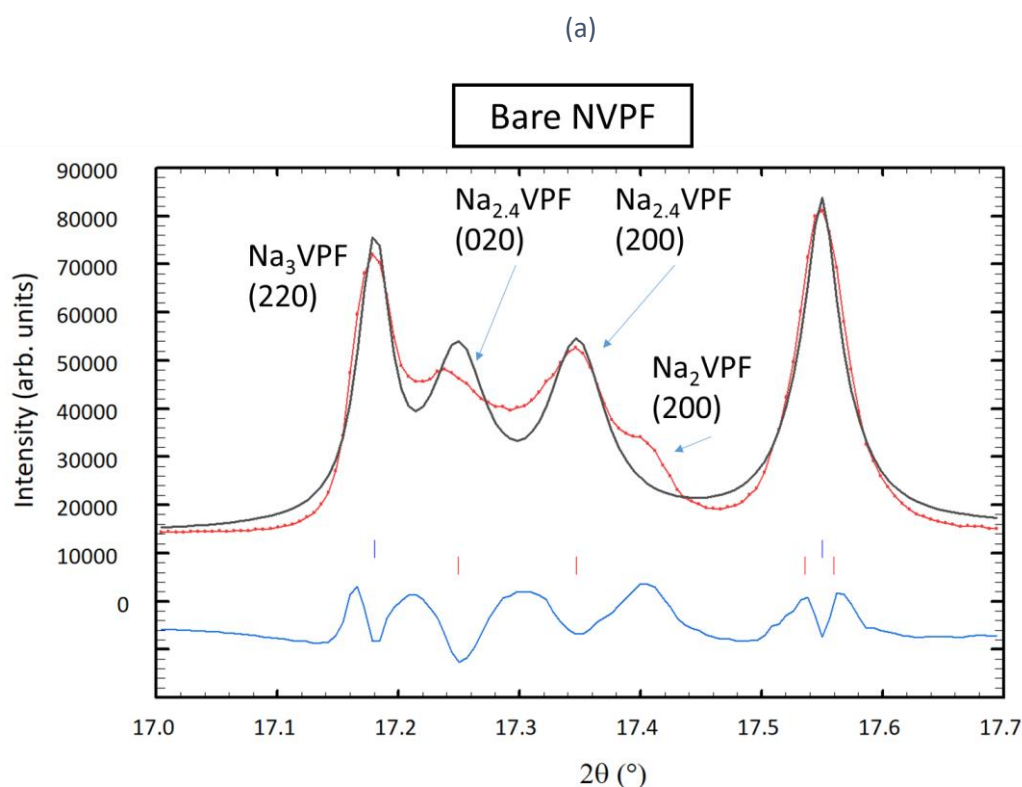
⁷ ALISTORE-ERI European Research Institute, FR CNRS 3104, F-80039 Amiens Cedex 1, France

*Corresponding author (L. Croguennec): Laurence.Croguennec@icmcb.cnrs.fr

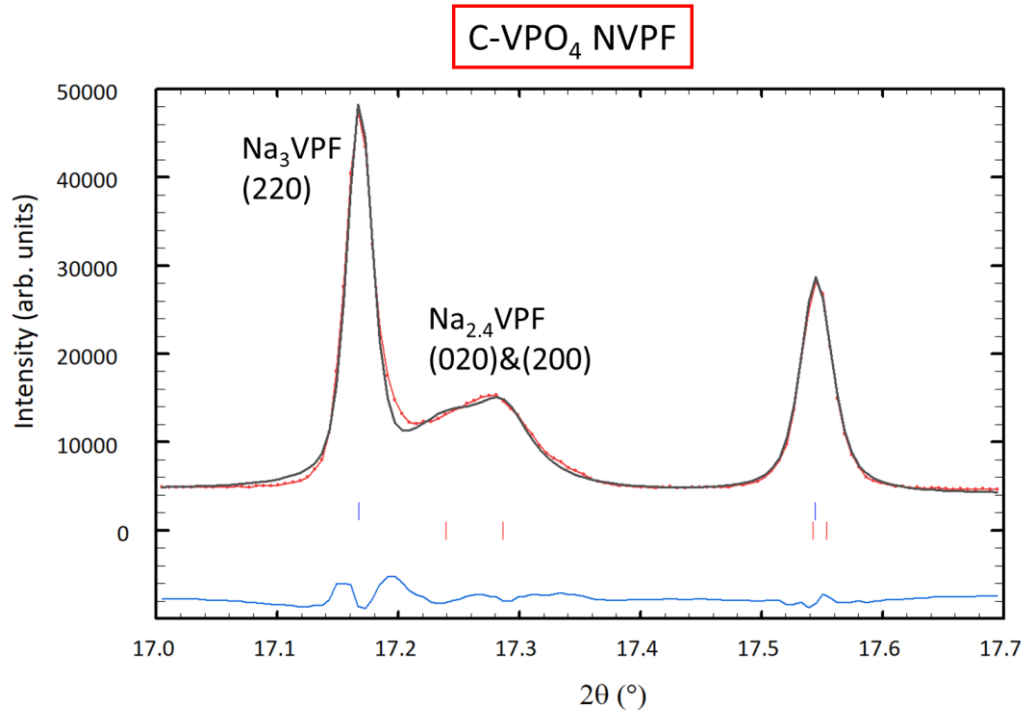
Figure 2 - additional information: Besides the cell parameters and the purity, crystallinity (*i.e.* the size of the crystalline domains) is also very similar for the three samples, as shown by the line widths at half maximum displayed in the table given hereafter.

	(333) FWHM	(006) FWHM
Bare NVPF	0.0449	0.0449
C-VPO ₄ NVPF	0.0351	0.0340
Coated NVPF	0.0309	0.0404

Figure S1: (a) Rietveld refinement of the SXRPD pattern #33 obtained during Na⁺ extraction from bare NVPF, enlargement of the selected angular range [17.0 - 17.7°(2θ)] highlighting the biphasic reaction between the initial phase Na₃VPF (40 wt.%) and the de-intercalated one Na_{2.4}VPF (60 wt.%). (b) Rietveld refinement of the SXRPD pattern #34 obtained during Na⁺ extraction from C-VPO₄ NVPF, enlargement of the selected angular range [17.0 - 17.7°(2θ)] highlighting the biphasic reaction between the initial phase Na₃VPF (40 wt.%) and the de-intercalated one Na_{2.4}VPF (60 wt.%). (c) Rietveld refinement of the SXRPD pattern #50 obtained during Na⁺ extraction from coated NVPF, enlargement of the selected angular range [17.0 - 17.7°(2θ)] highlighting the biphasic reaction between the initial phase Na₃VPF (30 wt.%) and the de-intercalated one Na_{2.4}VPF (70 wt.%).



(b)



(c)

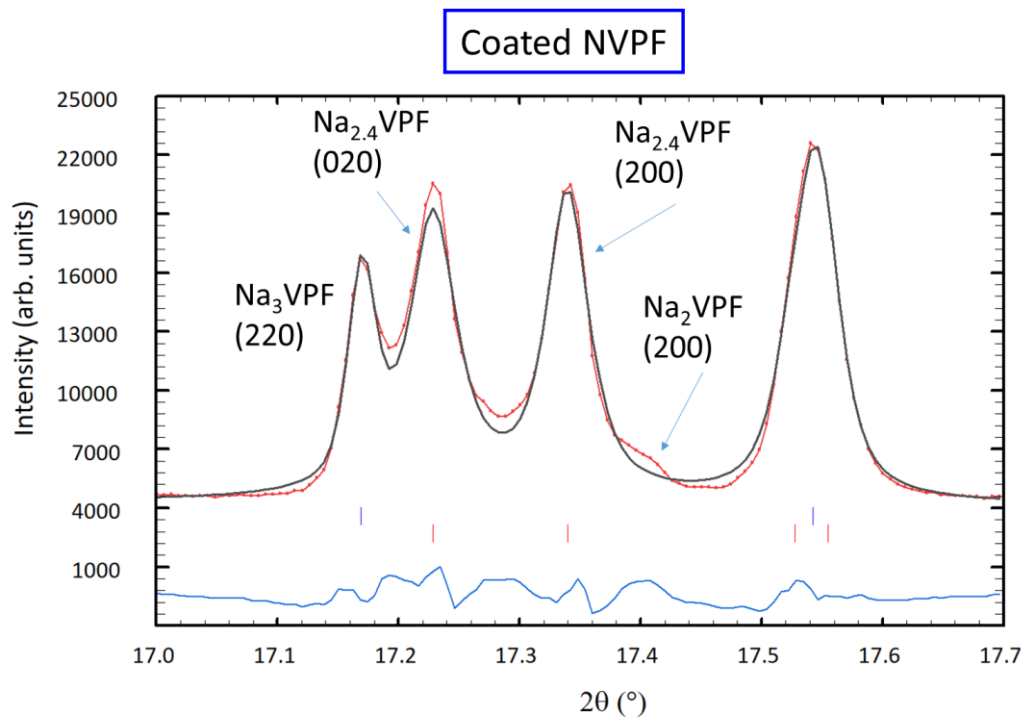


Figure S2: Electrochemical curve associated to the Na^+ de-intercalation from bare $\text{NVPF}_{2.8}\text{O}_{0.2}$, the SXRPD patterns reported in Figure 8 were collected *operando* during this experiment. Rietveld refinement of the pattern #21 considering a mixture of phases, the initial phase $\text{Na}_3\text{VPF}_{2.8}\text{O}_{0.2}$ (40 wt.%) and the de-intercalated one $\text{Na}_{3-x}\text{VPF}_{2.8}\text{O}_{0.2}$ (60 wt.%).

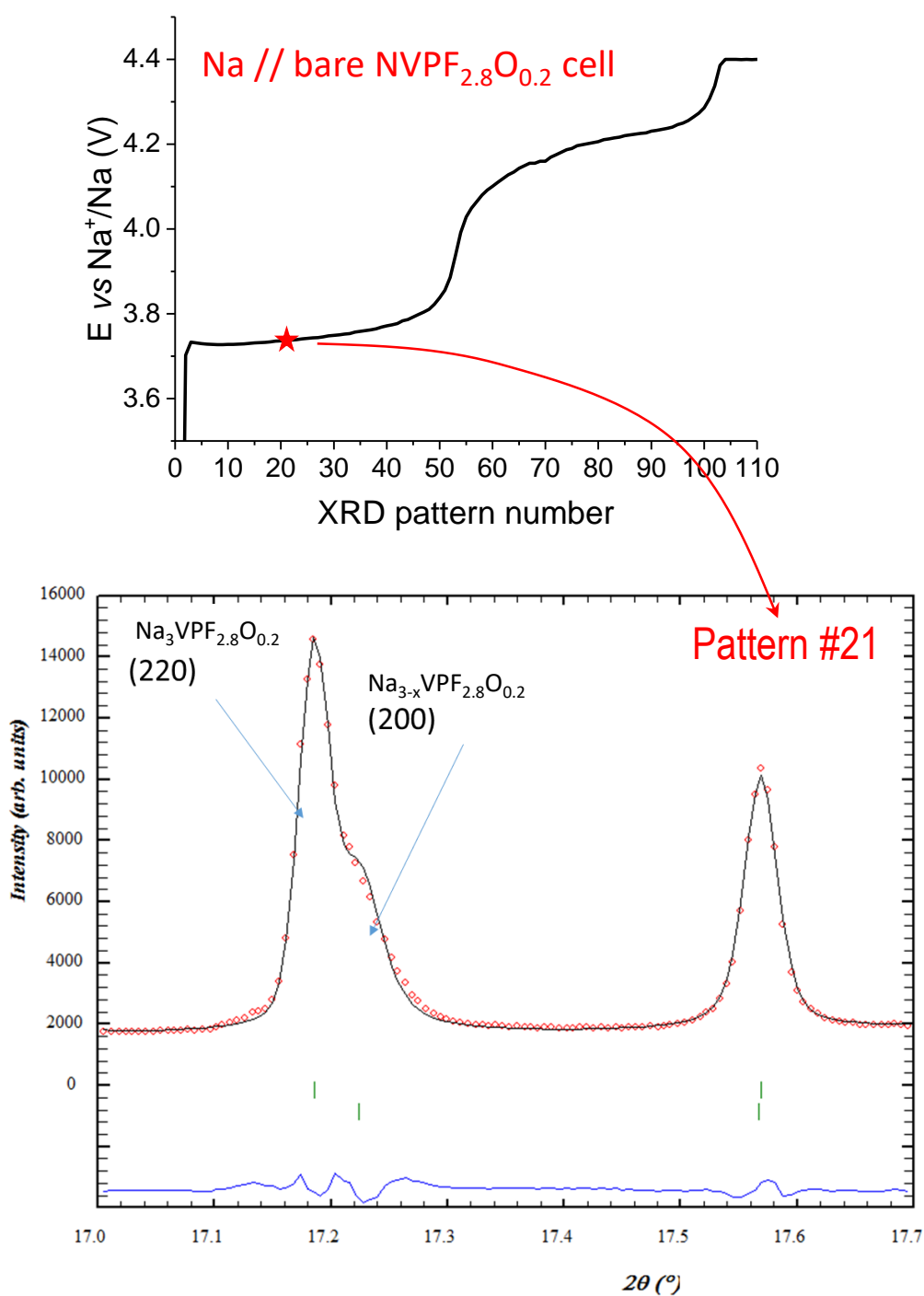


Table S1: Comparison of the cell parameters determined for the intermediate compositions stabilized upon cycling of coated NVPF versus Na metal, at C/10, and at room temperature or at low temperature (~ 0°C). These parameters were obtained from the analysis of the synchrotron X-ray powder diffraction data collected *operando* during the cycling of the batteries by the Rietveld method. The figures in red give for each parameter the variation induced by the decrease in temperature.

Cycling temperature of the cell Na//coated NVPF at C/10	Compositions			
	Na ₃ VPF	Na _{2.4} VPF	Na ₂ VPF	Na ₁ VPF
	Space group and Unit cell parameters (Å and Å ³)	Space group and Unit cell parameters (Å and Å ³)	Space group and Unit cell parameters (Å and Å ³)	Space group and Unit cell parameters (Å and Å ³)
RT	<i>Amam</i> $a = 9.0294(1)$ $b = 9.0448(1)$ $c = 10.7515(1)$ $V = 878.06(3) - V/Z = 219.52$ $b/a = 1.0017$	<i>Immm</i> (average) $a = 6.3254(1)$ $b = 6.3655(1)$ $c = 10.7766(1)$ $V = 433.91(3) - V/Z = 216.96$ $b/a = 1.0063$	<i>I4/mmm</i> (average) $a = 6.3057(1)$ $b = 6.3057(1)$ $c = 10.7976(1)$ $V = 429.33(3) - V/Z = 214.67$ $b/a = 1$	<i>Cmc2₁</i> $a = 8.7864(1)$ $b = 8.8021(1)$ $c = 11.0085(1)$ $V = 851.38(3) - V/Z = 212.84$ $b/a = 1.0018$
	<i>Amam</i> $a = 9.0272(1)$ $b = 9.0449(1)$ $c = 10.7493(1)$ $V = 877.68(3) - V/Z = 219.42$ $b/a = 1.0020$ <i>(-0.02%)</i> <i>(0.001%)</i> <i>(-0.02%)</i> <i>(-0.04%)</i>	<i>Immm</i> (average) $a = 6.3222(1)$ $b = 6.3682(1)$ $c = 10.7752(1)$ $V = 433.81(3) - V/Z = 216.91$ $b/a = 1.0072$ <i>(-0.05%)</i> <i>(0.04%)</i> <i>(-0.01%)</i> <i>(-0.02%)</i>	<i>I4/mmm</i> (average) $a = 6.3051(1)$ $b = 6.3051(1)$ $c = 10.7954(1)$ $V = 429.16(3) - V/Z = 214.58$ $b/a = 1$ <i>(-0.01%)</i> <i>(-0.01%)</i> <i>(-0.02%)</i> <i>(-0.04%)</i>	<i>Cmc2₁</i> $a = 8.7870(1)$ $b = 8.8027(1)$ $c = 11.0044(1)$ $V = 851.19(3) - V/Z = 212.80$ $b/a = 1.0018$ <i>(0.007%)</i> <i>(0.007%)</i> <i>(-0.04%)</i> <i>(-0.02%)</i>

Figure S3: Comparison of the first cycle of full cells versus hard carbon, the positive electrode materials being either C-VPO₄ NVPF or coated NVPF (current density of 12.8 mA/g in the potential window 2.0 - 4.3 V vs. hard carbon). The formulations of the positive and negative electrodes were 90/5/5 NVPF/SuperC65/PVDF/ and 92/3/5 HC/SuperC65/PVdF respectively.

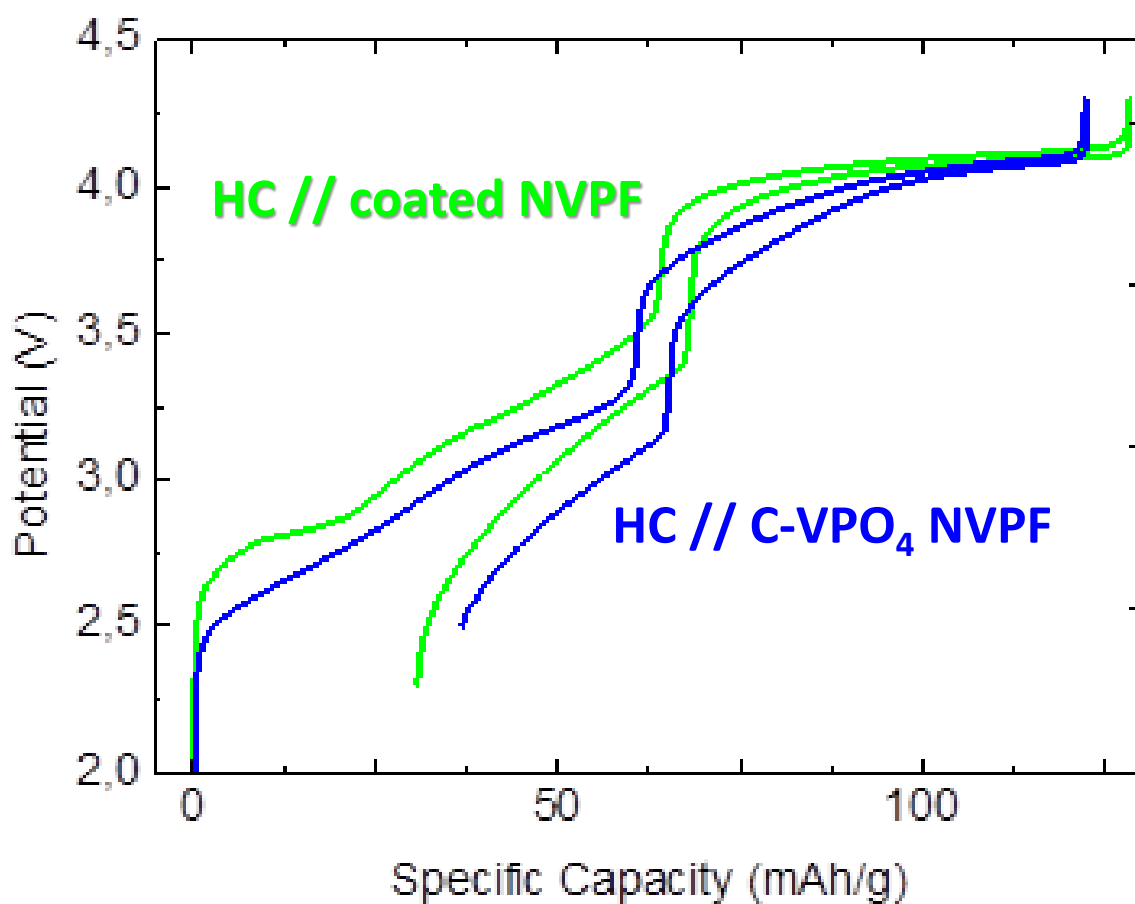


Figure S4: Voltage profiles as a function of the cell capacity during 18650 cells power rate capability tests, in charge (top) and discharge (bottom)

