Preparation of intergrown P/O-type biphasic layered oxides as a high-performance cathode for sodium ion batteries

Kai Wang[a,b,c,d], Zhen-Guo Wu[a,e*], Georgian Melinte[c*], Zu-Guang Yang[a], Abhishek Sarkar[c], Weibo Hua[g], Xiaoke Mu[c], Zu-Wei Yin[d], Jun-Tao Li[d], Xiao-Dong Guo[a,*], Ben-He Zhong[a], Christian Kübel[b,c,f*]

[a] *College of Chemical Engineering, Sichuan University, Chengdu 610065, China; E-mail: xiaodong2009@scu.edu.cn; zhenguowu@scu.edu.cn*

[b] *Department of Materials and Earth Sciences, Technical University Darmstadt, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany;*

[c] *Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, D-76344, Germany; E-mail: christian.kuebel@kit.edu; georgian.melinte@kit.edu*

[d] *College of Energy, Xiamen University, Xiamen 361005, China;*

[e] *College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.*

[f] *Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, D-76344, Germany;*

[g] *Institute for Applied Materials, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.*

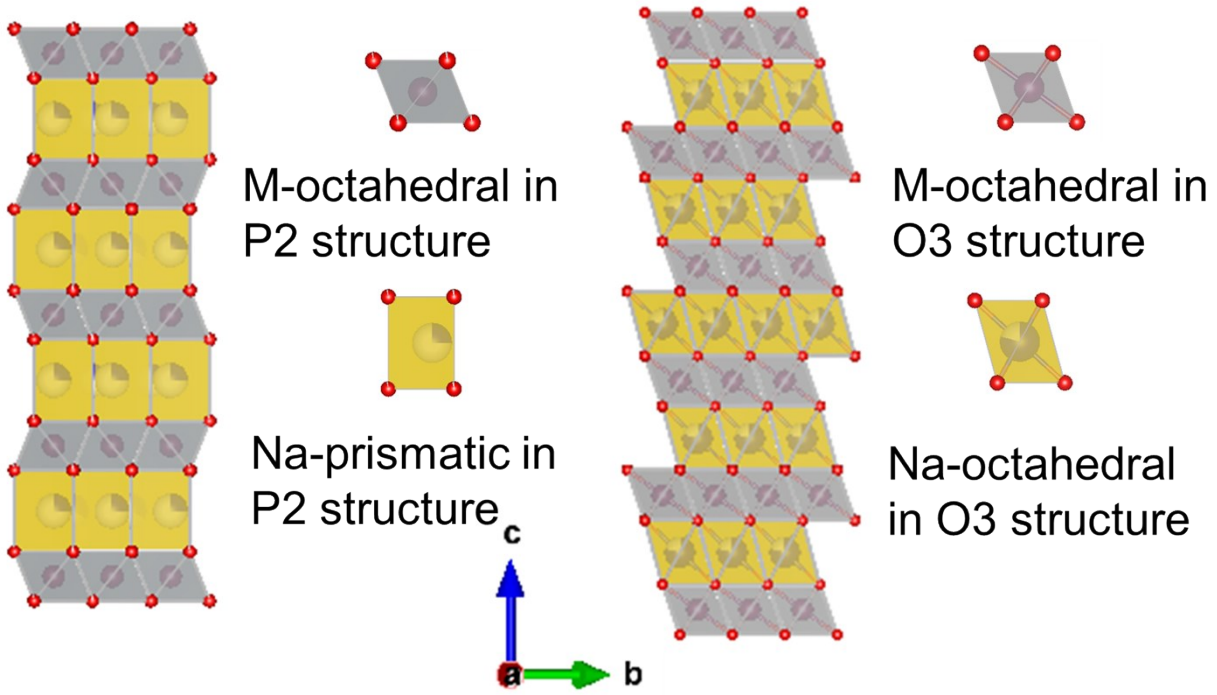

Figure S1: Projected structures of P2 and O3 phase.

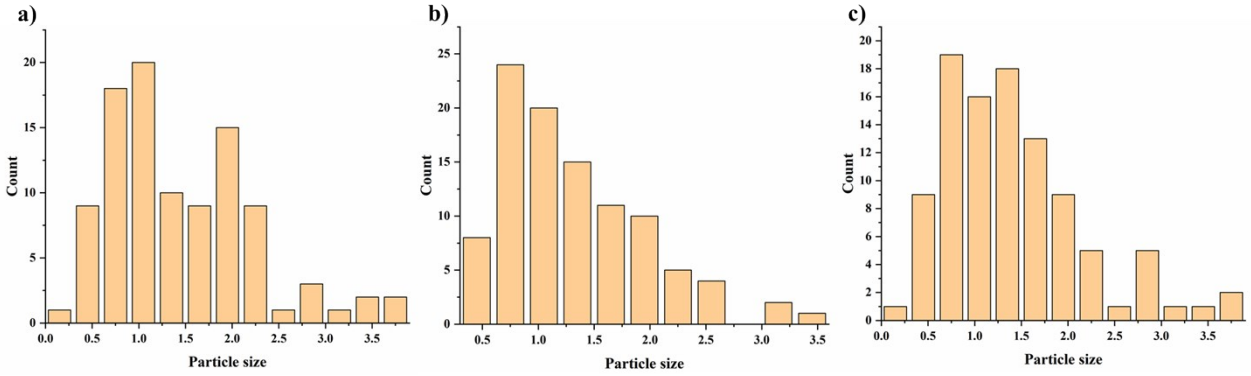

*Figure S2: Particle size statistics of the P2 (**a**), O3 (**b**) and P/O (**c**) biphasic material.*

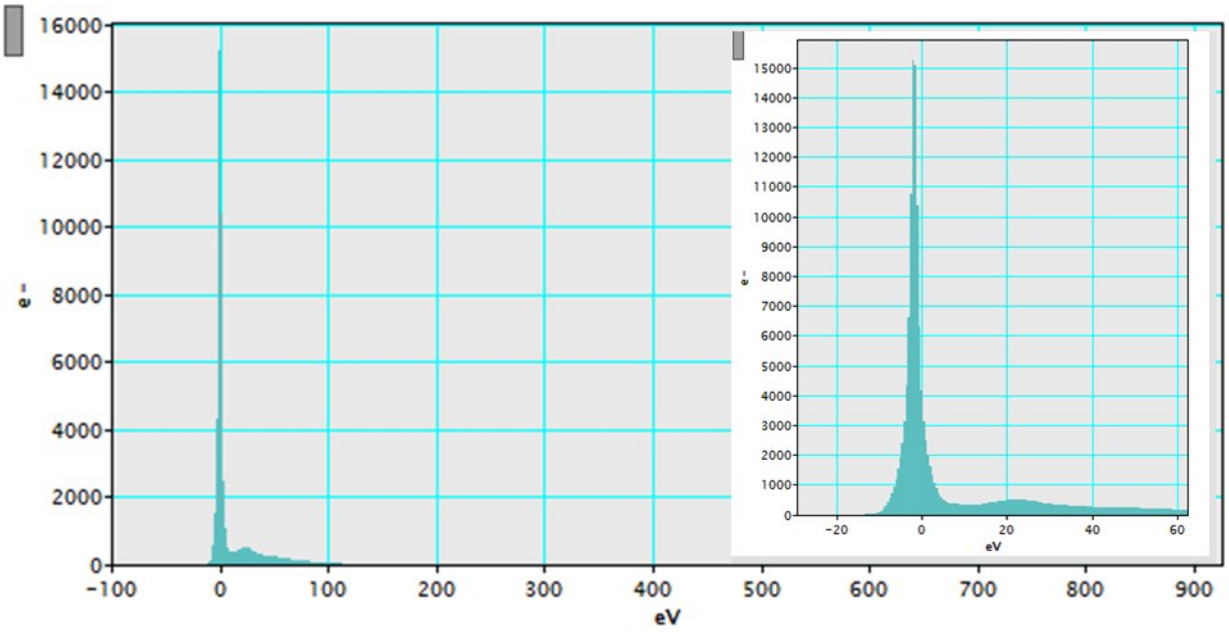

Figure S3 the EELS zero loss spectrum of FIB lamella, enlarged image of the energy range for zero loss peak and Plasmon peak was inserted.

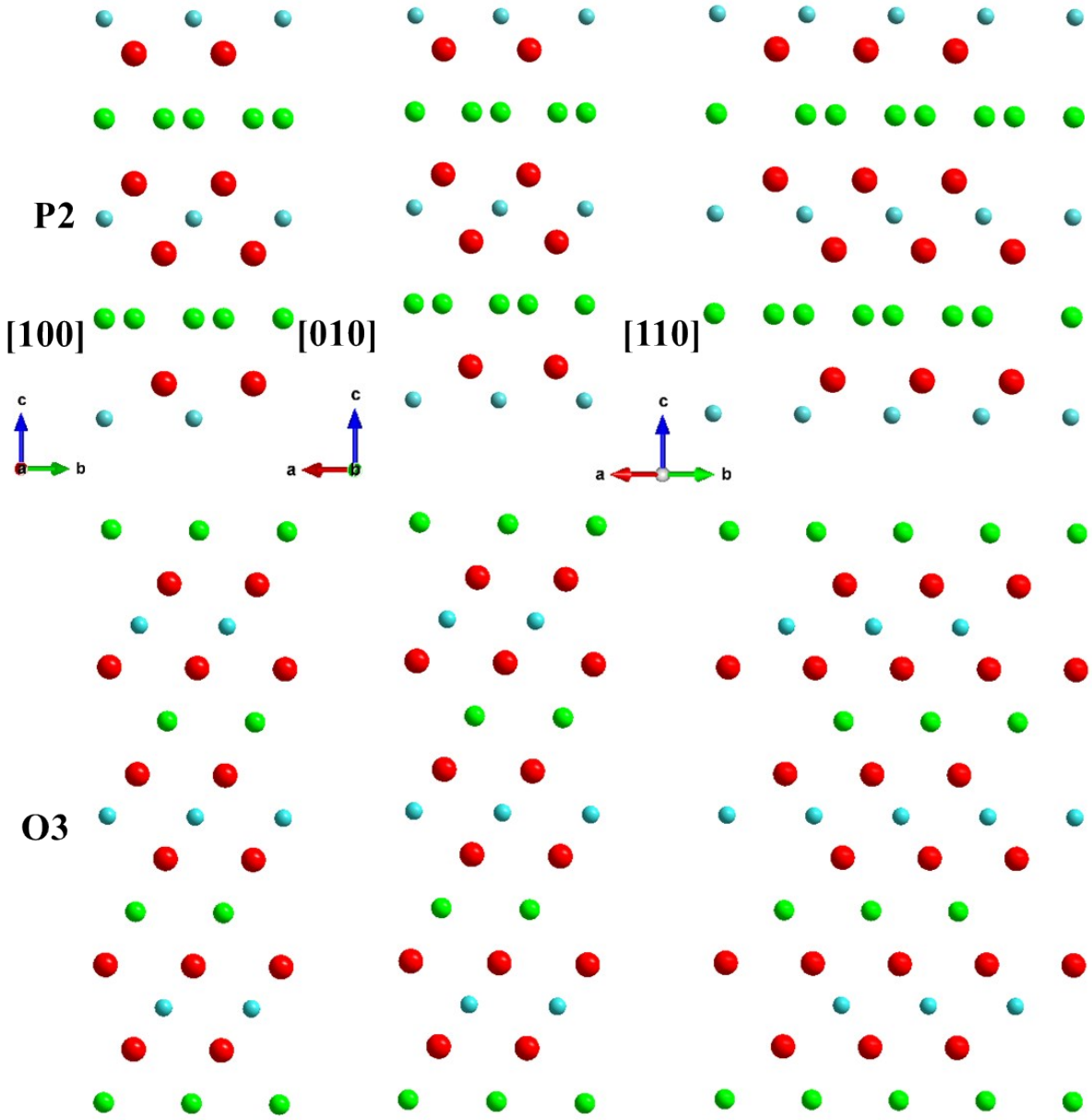

Figure S4: P2 and O3 structure along the [100], [010] and [110] directions: P2 (top) and O3 (bottom).

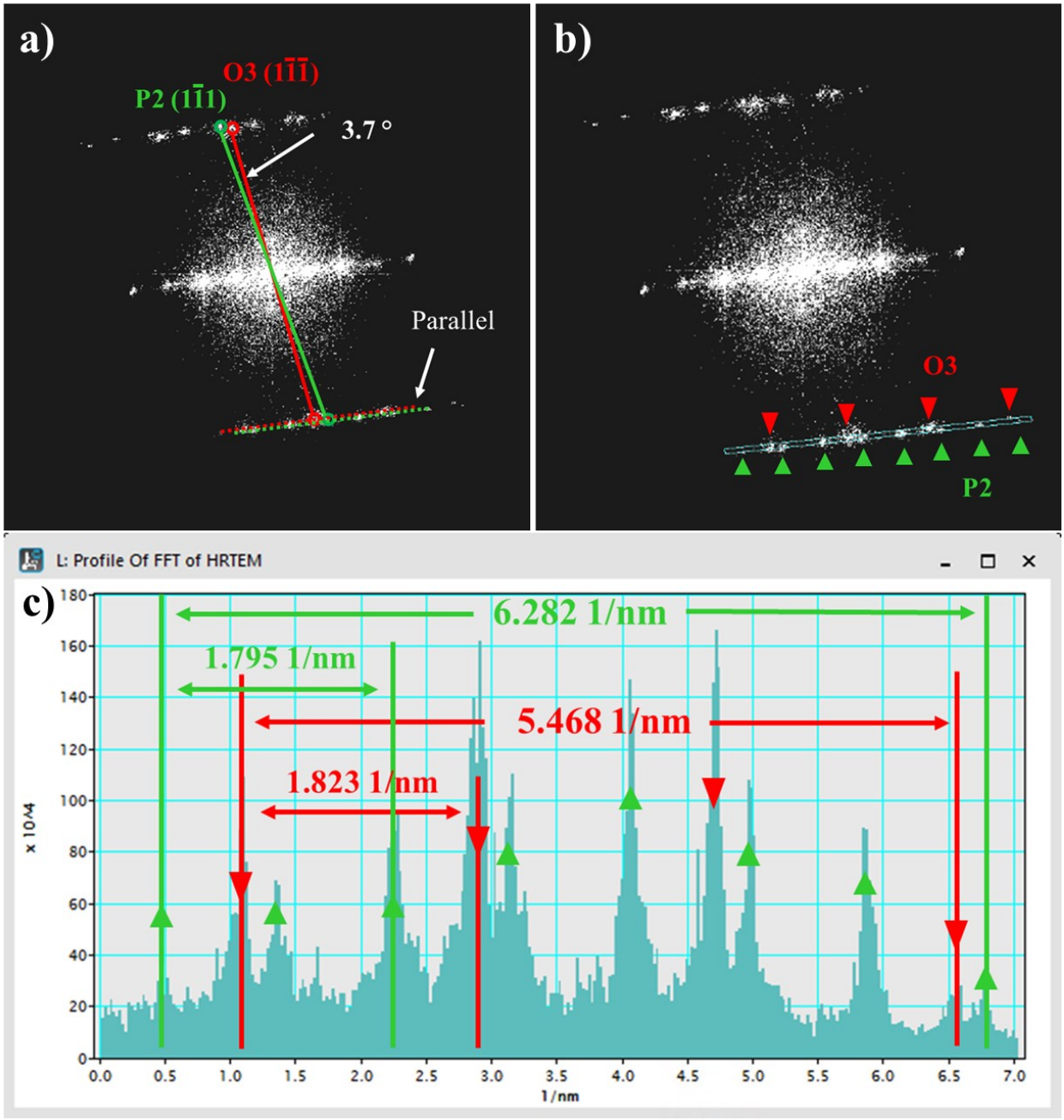

*Figure S5 Both **a** and **b** are the FFT of the HRTEM image in Fig. 3**c**; **c** is the profile of the line scan in marked area of **b**.*

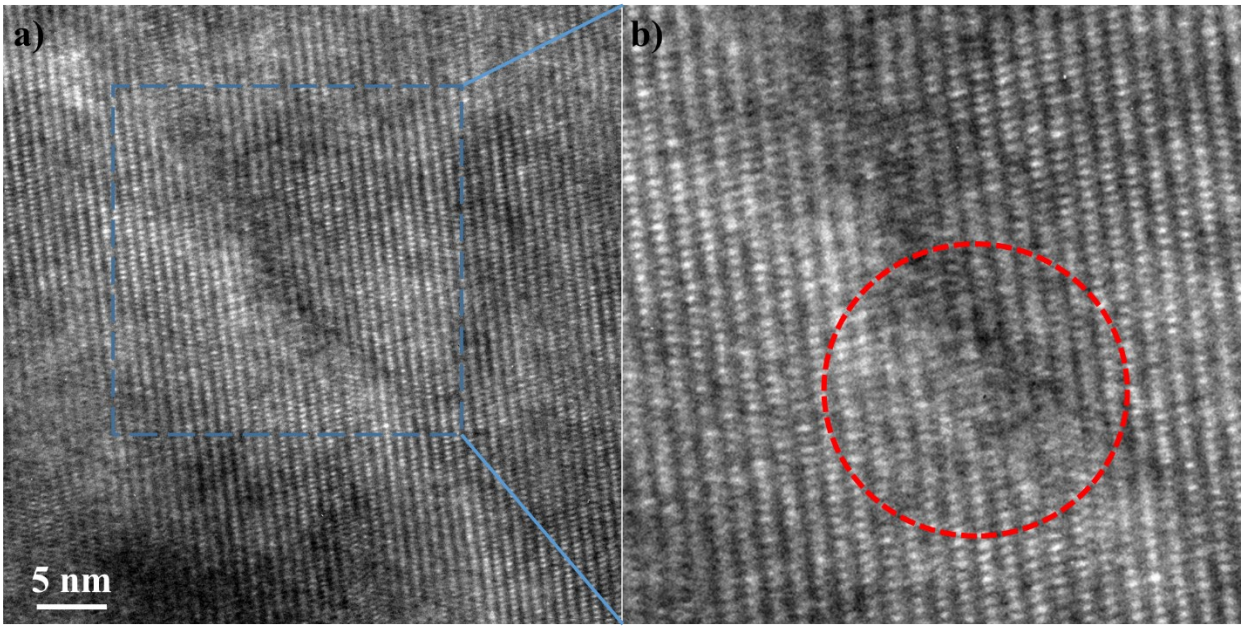

Figure S6 HRTEM image of the O3 area in the biphasic particle. ***b*** *is the enlarged area of the marked area in* ***a***.

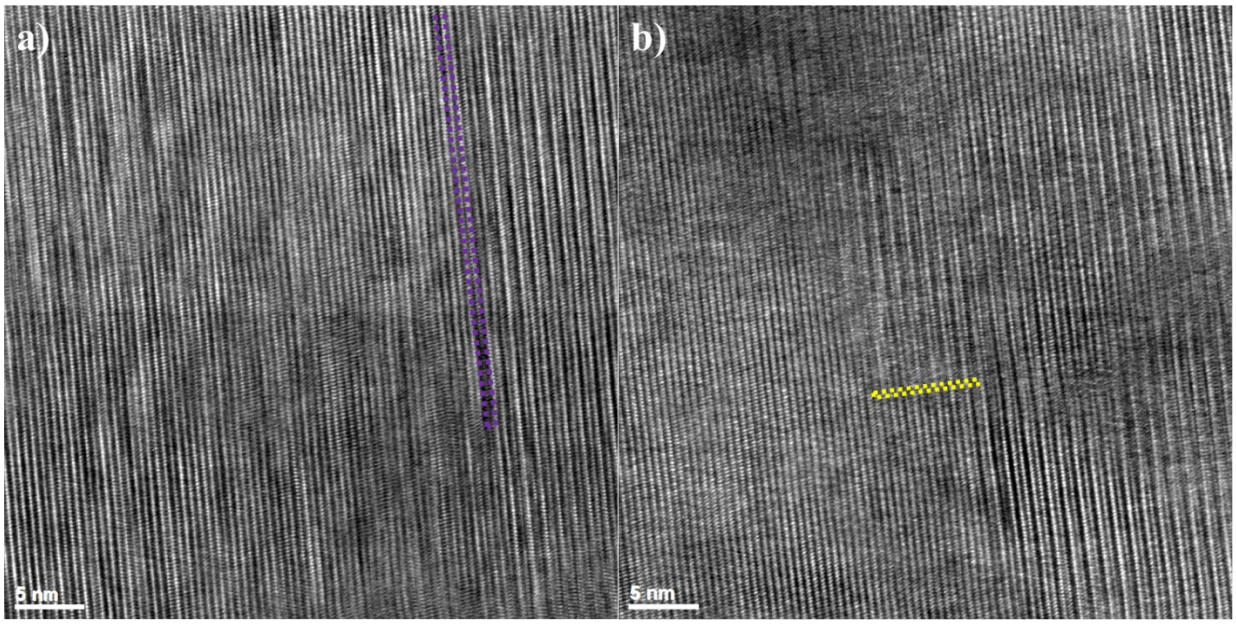

Figure S7 HRTEM images; the marked area in ***a*** *and* ***b*** *are the interfaces of 'D' type and 'E' type.*

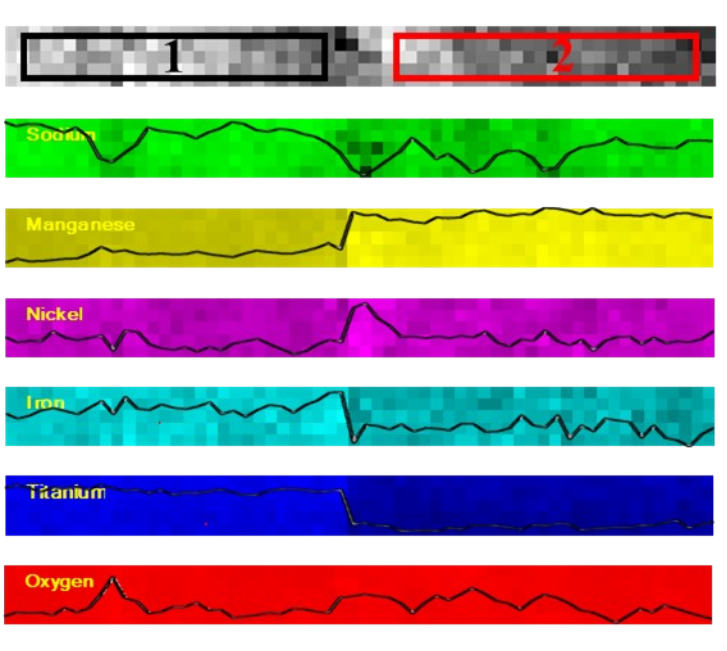

Figure S8 HAADF-STEM image and EELS map of the elemental distribution. The added line profiles correspond to the integrated element intensity.

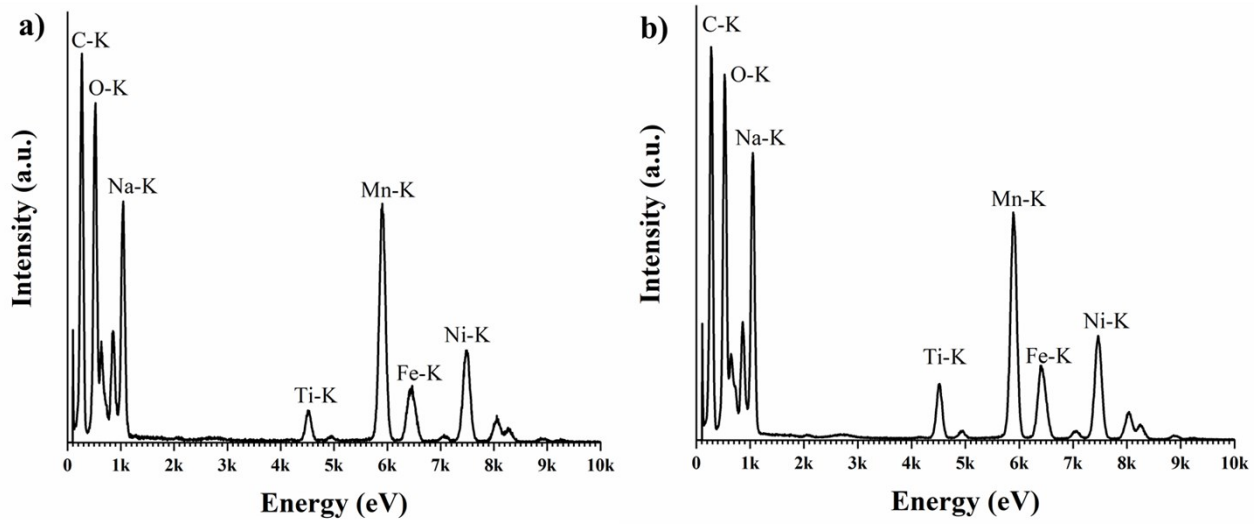

Figure S9: Integrated EDX spectrum of the O3 (a) and P2 (b) areas.

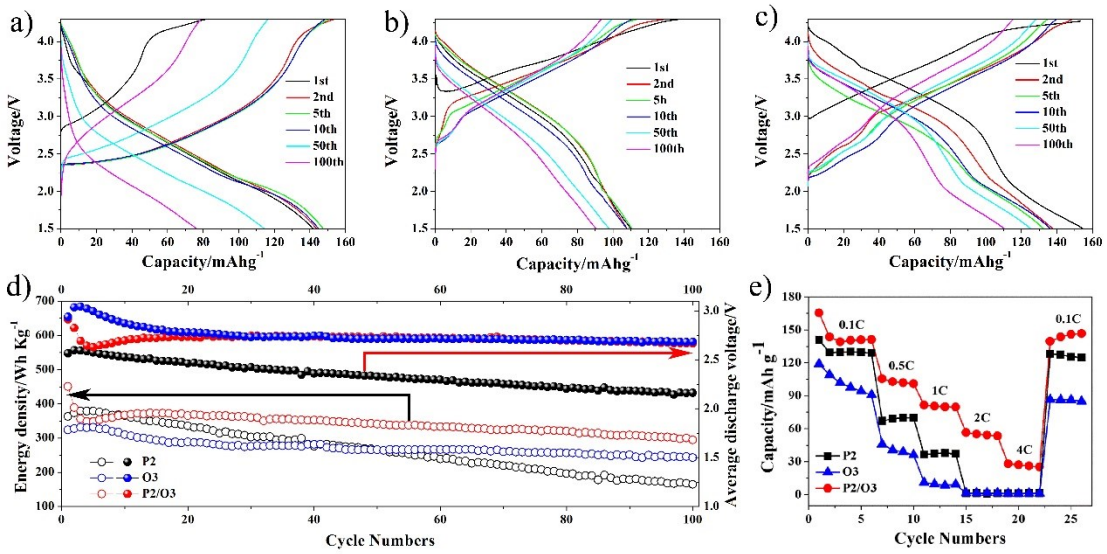

*Figure S10: Voltage-capacity plots for the 1st, 2nd, 5th, 10th, 50th, 100th cycles of the **a)** P2-type, **b)** O3-type, and **c)** P/O biphasic-type materials at 0.1C. **d)** Cycling performances of the average discharge voltage and energy density with increasing cycle number and **e)** rate performances of the three materials.*

Table S1: Crystallographic parameters of P2 material

Cell parameters

Space group: P63/mmc (194), a/b = 2.9107(0) Å, c = 11.1470(5) Å , V = 81.79(0) $Å^3$

Atomic position

Elements	site	x	y	z	occupancy
Na1	2b	0	0	1/4	0.28
Na2	2d	1/3	2/3	3/4	0.4
Mn	2a	0	0	0	0.55
Ni	2a	0	0	0	0.25
Fe	2a	0	0	0	0.1
Ti	2a	0	0	0	0.1
O	4f	1/3	2/3	0.088(4)	0.750(14)

Refinement parameters

Rp: 2.07% Rwp: 4.02% GOF: 3.81

For refining the data, the ICSD 93469 was used as the starting structure. In this case, only the z position of O and the occupancy were refined. The relative occupancy of sodium on 2b and 2d sites were refined, but, the overall amount of sodium was fixed to 0.68 as estimated from ICP. The amount of TM were also fixed with the estimated from ICP.

Table: S2 Crystallographic parameters of O3 material

Cell parameters

Space group: R-3 mH (166), a/b = 2.9314(1) Å, c = 16.4572(9) Å , V = 122.47(1) $Å^3$

Atomic position

Elements	site	x	y	z	occupancy
Na1	3a	0	0	0	1
Mn	3b	0	0	1/2	0.55
Ni	3b	0	0	1/2	0.25
Fe	3b	0	0	1/2	0.1
Ti	3b	0	0	1/2	0.1
O	6c	0	0	0.24	1

Refinement parameters

Rp: 2.57% Rwp: 4.33% GOF: 3.70

For refining the data, the ICSD 93469 was used as the starting structure. In this case, the best fit was obstained with sodium occupancy on the 3a site is close to 1 as estimated from ICP. The amount of TM were also fixed with the estimated from ICP. The O occupancy was also refined and was found close to one.

Table: S3 Crystallographic parameters of P/O biphasic material

	P2					O3				
Cell parameters	Space group: $P6_3/mmc$ (194), a/b = 2.9039(11)Å, c = 11.1307(10)Å, V = 81.29(9) Å^3					Space group: R-3mH (166), a/b = 2.9297(2)Å, c = 16.4870(2)Å, V = 122.55(2) Å^3				
Atomic position										
Elements	Site	x	y	z	Occupancy	Site	x	y	z	Occupancy
Na1	2b	0	0	1/4	0.28	3a	0	0	0	1
Na2	2d	1/3	2/3	3/4	0.40					
Mn	2a	0	0	0	0.55	3b	0	0	1/2	0.55
Ni	2a	0	0	0	0.25	3b	0	0	1/2	0.25
Fe	2a	0	0	0	0.1	3b	0	0	1/2	0.1
Ti	2a	0	0	0	0.1	3b	0	0	1/2	0.1
O	4f	1/3	2/3	0.077(5)	0.95	6c	0	0	0.260(2)	1
Ratio(wt%)				73.1(12)					26.9(12)	
Refine parameters										
Rexp: 1.05% Rwp: 5.62% Rp : 3.14										

In this case, the starting P2 and O3 structure were similar with the single structures from obtained from the afore-mentioned refinements.