Supporting information

Critical design factors for kinetically favorable P-based compounds toward the alloying with Na ions for high-power sodium-ion batteries

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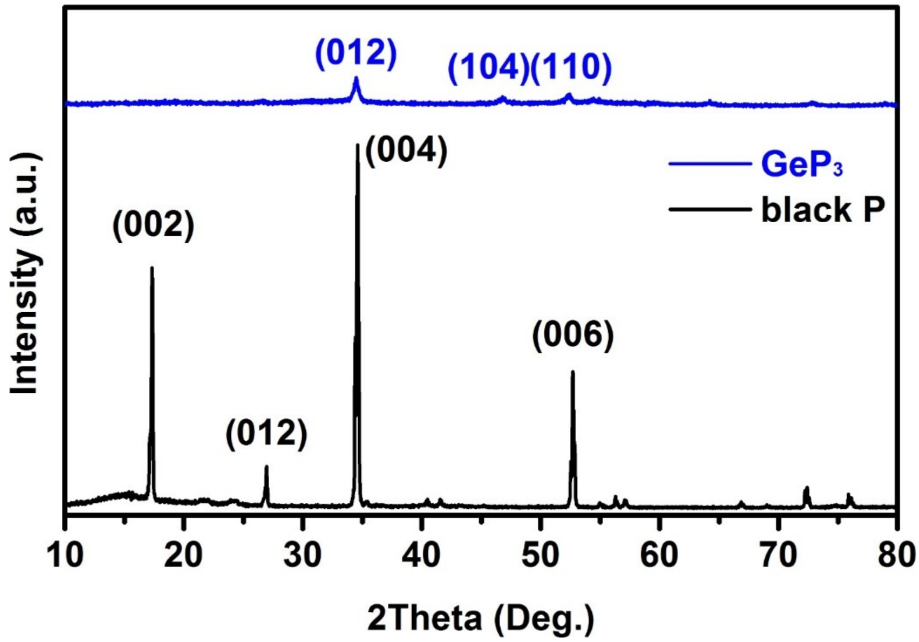

Figure S1. XRD patterns of black P and GeP_3.

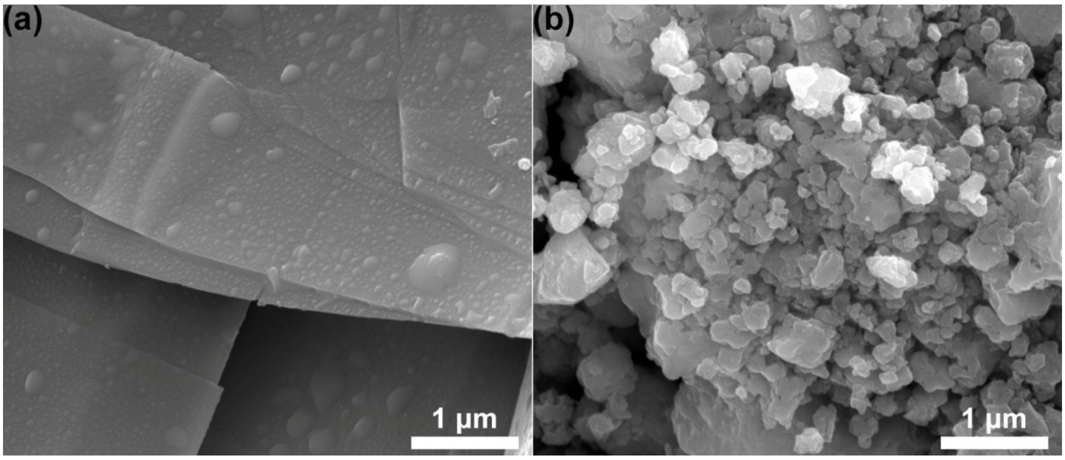

Figure S2. SEM images of pristine black P (a) and GeP_3 (b).

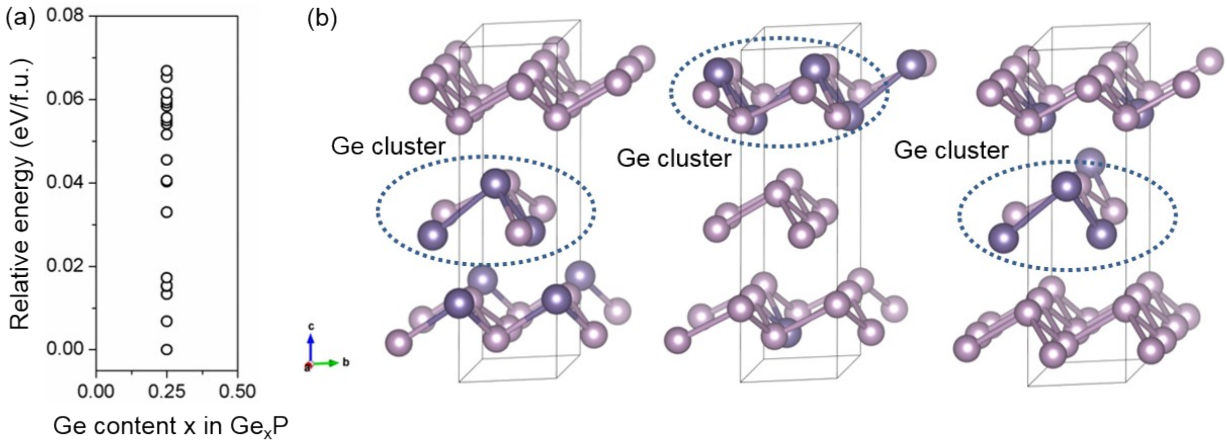

Figure S3. (a) Relative energies considering all possible Ge/P atomic configurations at Ge content x in Ge_xP. (b) Sampled GeP_3 atomic models at thermodynamically unstable states compared to the GeP_3 structure at the ground state (Figure 1a).

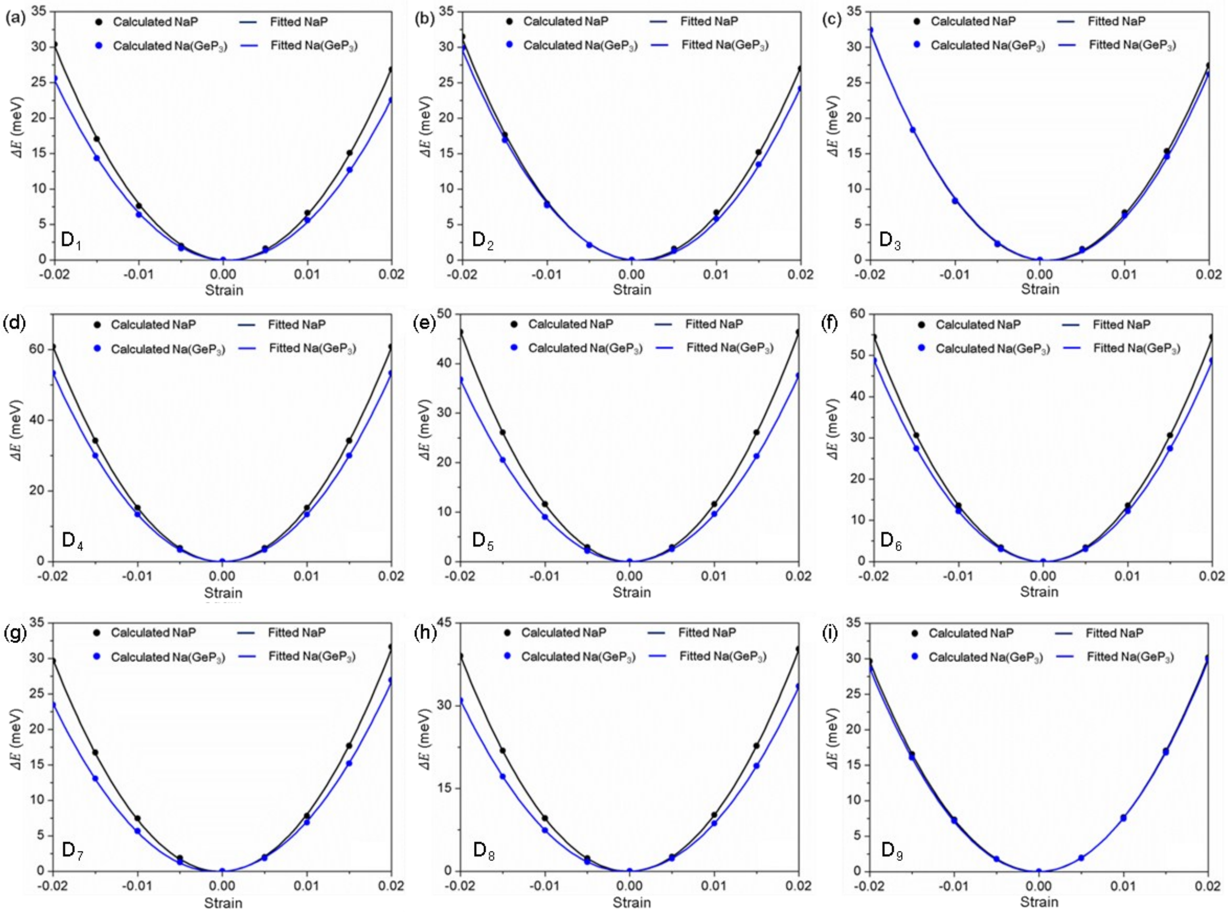

Figure S4. Strain energies as a function of small strain ($-0.02 \leq \delta \leq 0.02$), depending on distortion matrices (D_1 to D_9, see Table S2) to obtain the nine independent elastic constants (C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, C_{23}, which are summarized in Table S1) as shown in Figure 1b.[1]

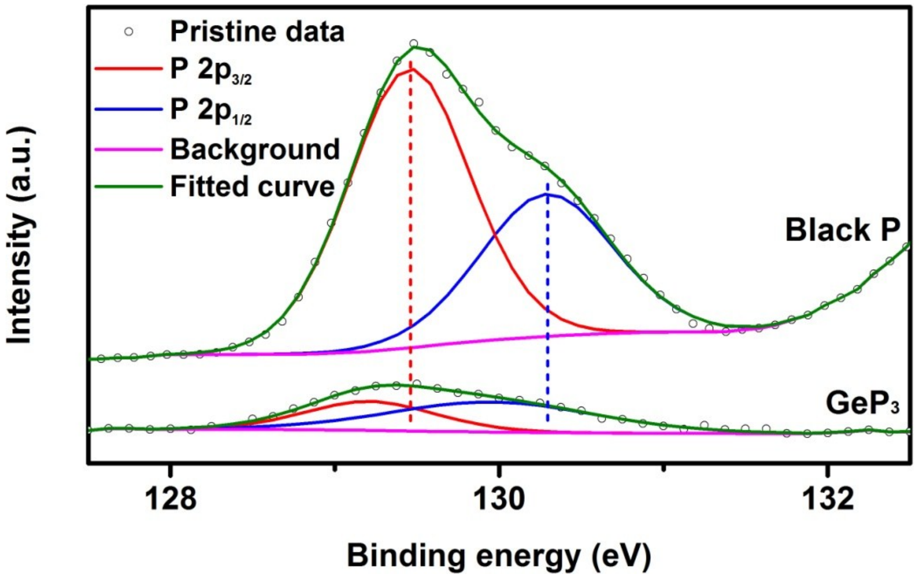

Figure S5. XPS spectra of pristine GeP_3 and black P.

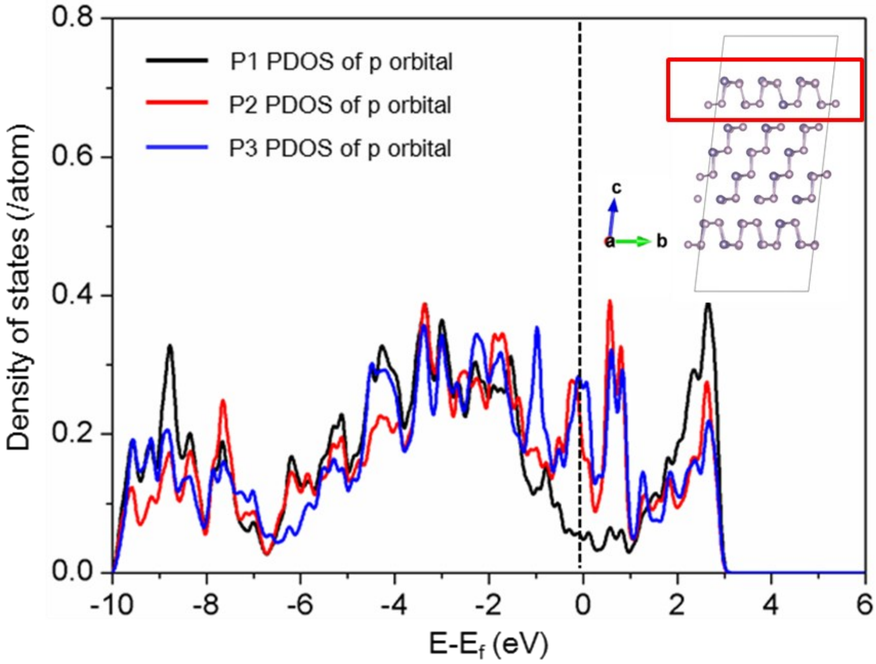

Figure S6. Partial density of states of P 3*p*-electron in the GeP_3 surface, described within the highlighted red box in the inset, depending on the three types of P as shown in Figure 2a.

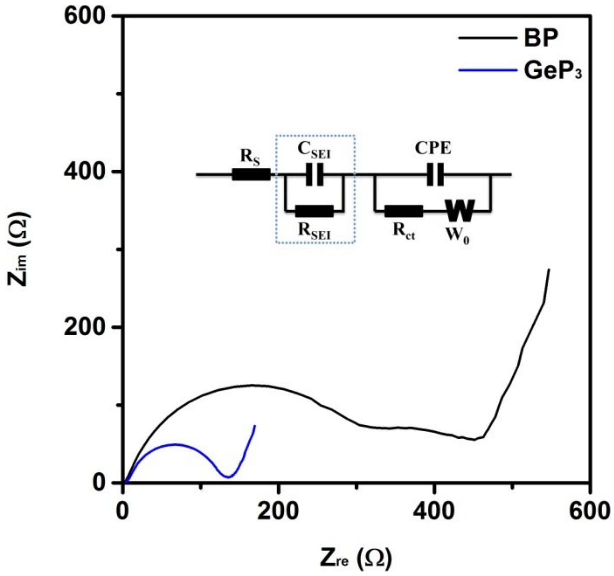

Figure S7. Impedance spectra of GeP_3 and black P electrodes at fully discharged state.

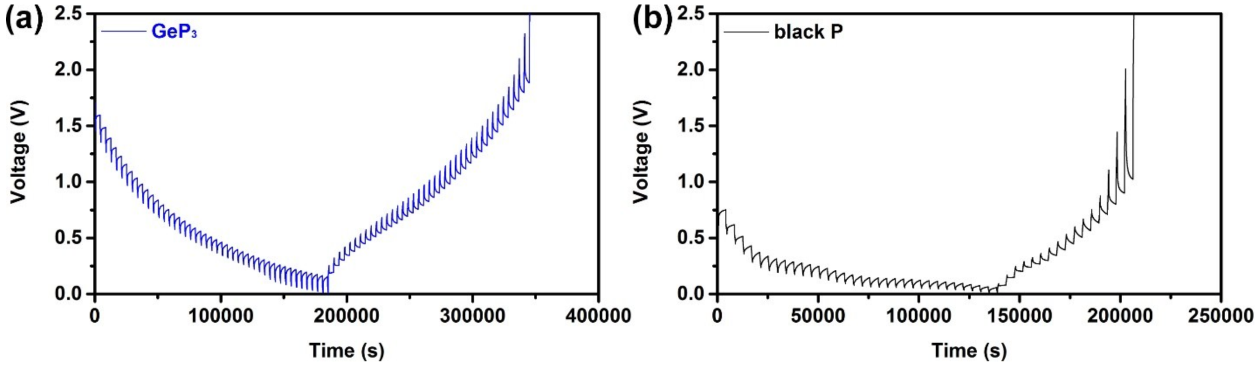

Figure S8. GITT profiles of the GeP_3(a) and BP (b) electrodes.

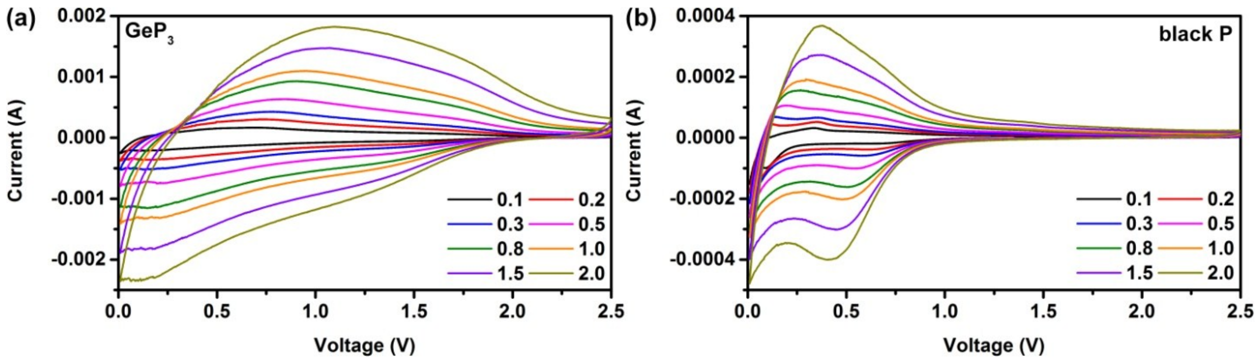

Figure S9. CV curves at different scan rates of GeP_3(a) andblack P (b).

Table S1. Calculated nine independent elastic constants (C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55}, and C_{66}) for NaP and $Na(GeP_3)$.

Compound	Elastic constants (GPa)								
	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}
$Na(GeP_3)$	52.891	59.329	64.308	28.429	23.175	29.716	29.285	20.425	26.793
NaP	65.689	67.085	68.710	31.230	21.711	33.607	34.878	26.617	31.252

Table S2. Distortion matrices for an orthorhombic system.

Distortion matrices		
$D_1 = \begin{pmatrix} 1+\delta & 0 & 0 \\ 0 & 1+\delta & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$D_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1+\delta & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$D_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\delta \end{pmatrix}$
$D_4 = \begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & \frac{\delta}{(1-\delta^2)^{1/3}} \\ 0 & \frac{\delta}{(1-\delta^2)^{1/3}} & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$D_5 = \begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & \frac{\delta}{(1-\delta^2)^{1/3}} \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ \frac{\delta}{(1-\delta^2)^{1/3}} & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$D_6 = \begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & \frac{\delta}{(1-\delta^2)^{1/3}} & 0 \\ \frac{\delta}{(1-\delta^2)^{1/3}} & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$
$D_7 = \begin{pmatrix} \frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$D_8 = \begin{pmatrix} \frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$D_7 = \begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1+\delta}{(1+\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} \end{pmatrix}$

Reference

1. P. Ravindran, L. Fast, P. A. Korzhavyi, B. Johansson, J. Wills and O. Eriksson, *J. Appl. Phys.*, 1998, **84**, 4891-4904.