——Supporting Information——

# Rational Design of Mixed Polyanion Electrodes $Na_xV_2P_{3-i}(Si/S)_iO_{12}$ for Sodium Batteries

Vishakha Kapoor,[1#] Baltej Singh,[1#] Gopalakrishnan Sai Gautam,[2] Anthony K. Cheetham,[1,3] and Pieremanuele Canepa[1,4] *

[1]Department of Materials Science and Engineering, National University of Singapore, 117575, Singapore

[2]Department of Materials Engineering, Indian Institute of Science, Bengaluru, 560012, Karnataka, India

[3]Materials Department and Materials Research Laboratory,

University of California, Santa Barbara, California 93106, United States

[4]Chemical and Biomolecular Engineering, National University of Singapore,

4 Engineering Drive 4, Singapore, 117585

*pcanepa@nus.edu.sg

[#]These authors contributed equally

## S1 Formation Energy Diagram of NaSICON $Na_xV_2(PO_4)_3$

From the density functional theory (DFT) total energies we predicted the formation energies $E_f$ of each structure of $Na_xV_2P_{3-i}(Si/S)_iO_{12}$ ($Na_xVP_{3-i}(Si/S)_i$) ranging from x = 0 to 4, with respect to the end member states of $Na_0VP_{3-i}(Si/S)_i$ and $Na_4VP_{3-i}(Si/S)_i$, respectively. For example, the formation energy of each structure of $Na_xVP_3$ can be calculated as in **Eq. S1**:

$$E_f(x) = E[Na_xV_2P_3O_{12}] - \left(\frac{4-x}{4}\right)E[V_2P_3O_{12}] - \left(\frac{x}{4}\right)E[Na_4V_2(PO_4)_3] \qquad \text{(S1)}$$

From **Eq. S1**, positive formation energies indicate phase separation of $Na_xVP_3$ into the end member structures, i.e., $Na_1VP_3$ and $Na_4VP_3$. The envelop of points formed by connecting the points with the lowest formation energy ——the ground state structures— forms the so-called pseudo-binary convex hull (pseudo-binary, since the Na-content is the only compositional variable that is allowed to change). Structures above the pseudo-binary convex hull are deemed metastable or unstable, with respect to the pseudo-binary ground states.

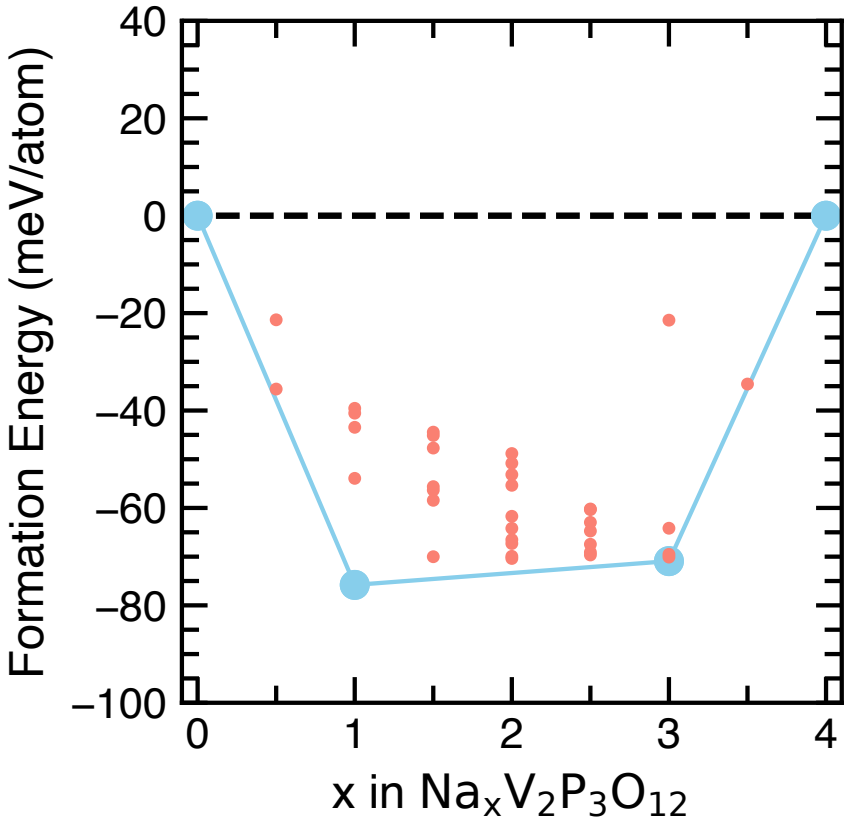


**Figure S1** Hubbard *U* corrected density functional theory (DFT+*U*) computed convex hull of $Na_xV_2(PO_4)_3$ vs. Na content (x; $0 < x < 4$). Blue dots represent stable entries compositions, and the red dots represents the metastable or unstable orderings at various concentrations of Na in pseudo-binary $Na_xV_2(PO_4)_3$.

## S2 Ground State Orderings of $Na_xV_2(PO_4)_3$

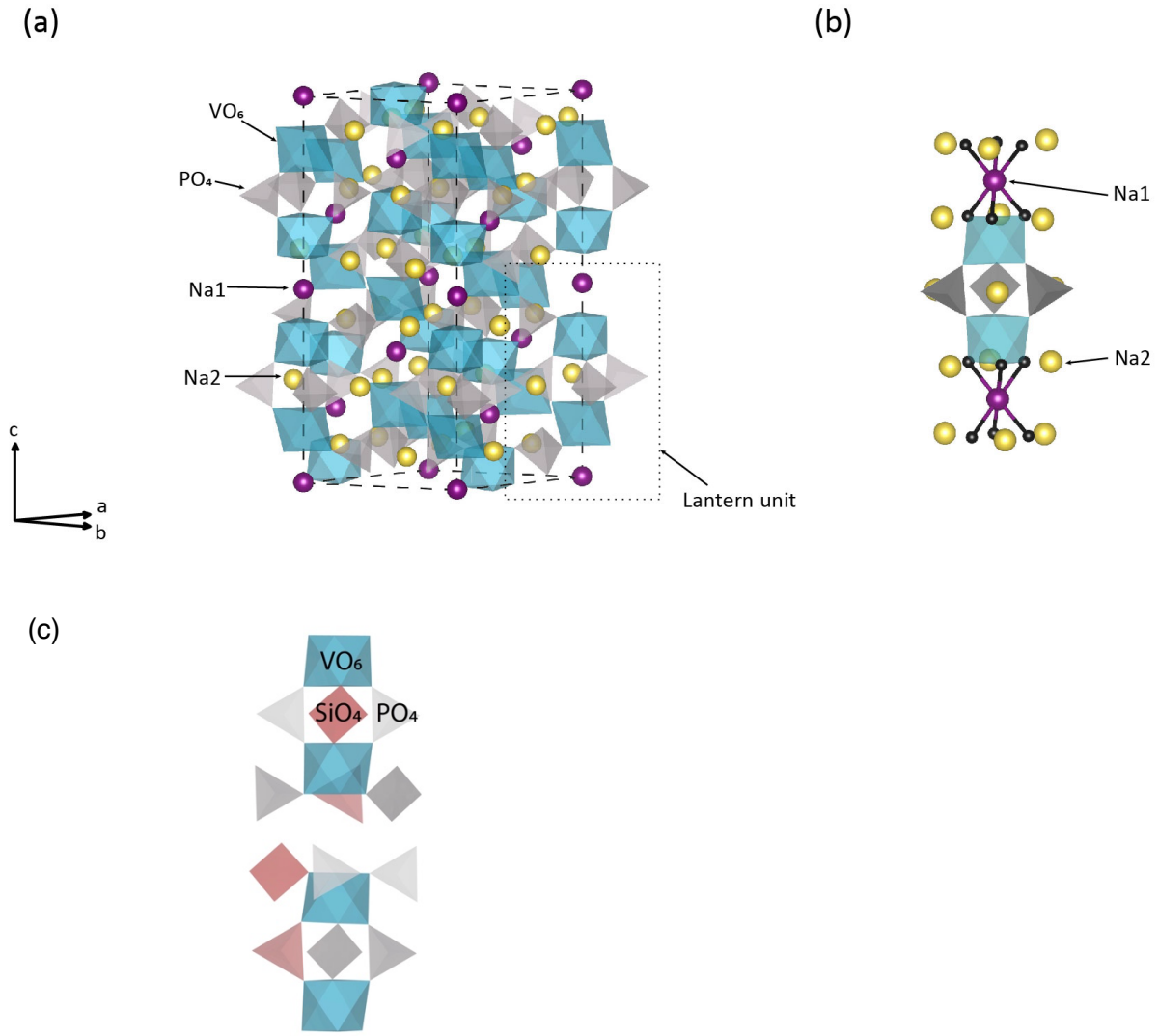


**Figure S2** (a) The rhombohedral ($R\bar{3}c$) structure of $Na_4M_2(PO_4)_3$. The "lantern unit" is made up of two $MO_6$ octahedra (cyan) sharing corners with $PO_4^{-3}$ tetrahedra (grey). The box in (a) highlights the arrangement of the lantern units. Two distinct Na ions, i.e., Na1 (violet) and Na2 (yellow), are present in the rhombohedral NaSICONs. Panel (b) shows the Na ordering around the lantern units in the rhombohedral unit cell. (c) Framework of $Na_xV_2P_2Si_1O_{12}$ showing the two lanterns of the primitive unit cell, each containing one $SiO_4^{4-}$ tetrahedron (pink) and two $PO_4^{3-}$ tetrahedra (grey) corner-sharing oxygen with two $VO_6$ octahedra (cyan).

## S2 Formation Energy Diagrams of NaSICON $Na_xV_2P_iSi_{3-i}O_{12}$

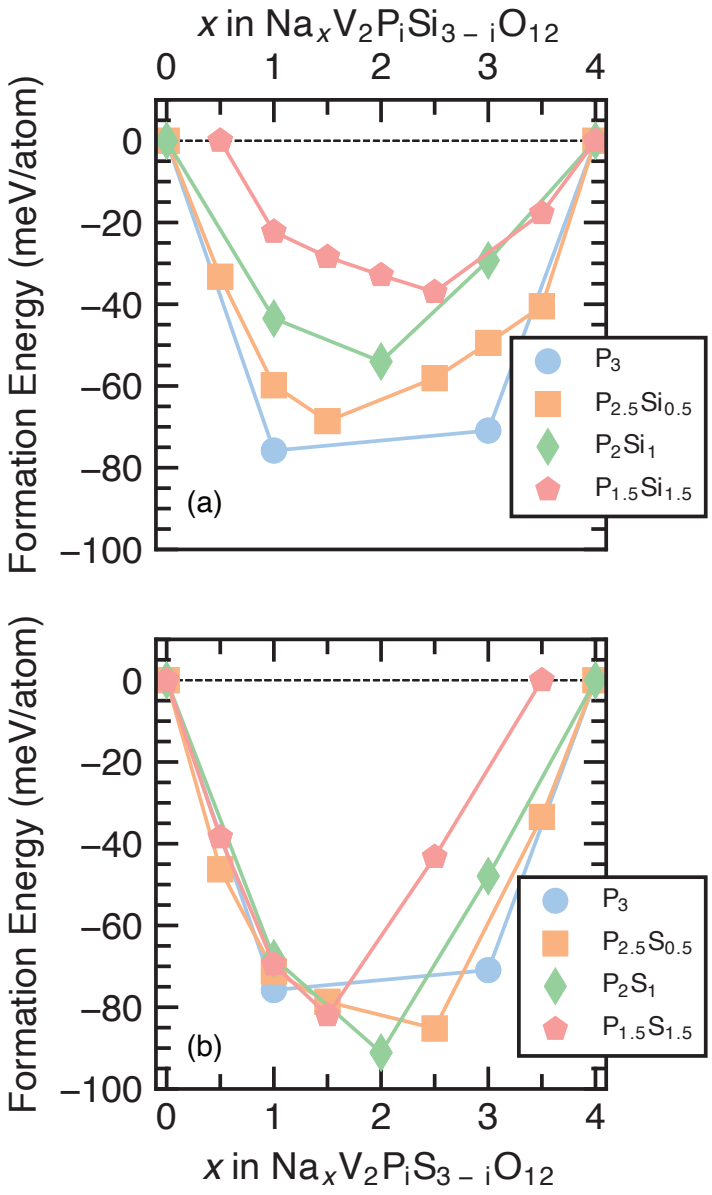


**Figure S3** DFT+*U* computed convex hull of $Na_xV_2P_i(Si/S)_{3-i}O_{12}$ for $0 < x < 4$. Only the ground state orderings at various concentrations of Na are displayed.

## S3 Decomposition Reactions of NaSICON $Na_xV_2P_iSi_{3-i}O_{12}$

**Table S1** DFT computed reaction energies and corresponding dissociation products of $Na_xV_2P_i(Si)_{3-i}O_{12}$.

| | Reaction | Energy (eV/atom) | $E^{hull}$ ( eV/atom) |
|---|---|---|---|
| **0** | 0.2 Na2V3P2O13 + 0.2 NaV3P2O13 + 0.4 NaV2(PO4)3 + SiO2 -> NaV2Si(PO6)2 | 0.797338832 | 0.044296602 |
| **1** | 0.2 Na2VPO6 + 0.4 NaV3P2O13 + 0.2 NaV3O8 + 2 SiO2 -> NaV2Si2PO12 | 1.391227828 | 0.077290435 |
| **2** | NaV2(PO4)3 + SiO2 + 2 VPO5 -> NaV4SiP5O24 | 1.118329775 | 0.031952279 |
| **3** | 0.5 NaV3P2O13 + 0.5 NaV2(PO4)3 + 2 SiO2 + 1.5 VPO5 -> NaV4Si2(PO6)4 | 1.886448466 | 0.053898528 |
| **4** | NaV3P2O13 + 3 SiO2 + VPO5 -> NaV4Si3(PO8)3 | 2.487636407 | 0.071075326 |
| **5** | SiO2 + 2 NaVPO5 -> Na2V2Si(PO6)2 | 0.909462035 | 0.047866423 |
| **6** | NaVO3 + 2 SiO2 + NaVPO5 -> Na2V2Si2PO12 | 1.625797193 | 0.085568273 |
| **7** | 0.2 Na2V3P2O13 + 0.2 NaV3P2O13 + 1.4 NaV2(PO4)3 + SiO2 -> Na2V4SiP5O24 | 0.799252096 | 0.022201447 |
| **8** | 0.6 Na2V3P2O13 + 0.6 NaV3P2O13 + 0.2 NaV2(PO4)3 + 3 SiO2 -> Na2V4Si3(PO8)3 | 2.305235779 | 0.064034327 |
| **9** | 0.5 NaV(SiO3)2 + 0.3333 Na4VP2O9 + 0.1667 Na3V3(PO4)4 + 0.6667 NaVPO5 -> Na3V2Si(PO6)2 | 0.588900858 | 0.029445043 |
| **10** | 0.3846 NaV(SiO3)2 + 0.4615 Na4VP2O9 + 1.231 SiO2 + 0.07692 NaVPO5 + 0.07692 Na9V14O35 -> Na3V2Si2PO12 | 0.939653696 | 0.046982685 |
| **11** | NaV2(PO4)3 + SiO2 + 2 NaVPO5 -> Na3V4SiP5O24 | 0.916105635 | 0.024759612 |
| **12** | 0.5 Na2V3P2O13 + 0.5 NaV2(PO4)3 + 2 SiO2 + 1.5 NaVPO5 -> Na3V4Si2(PO6)4 | 1.767993387 | 0.047783605 |
| **13** | Na2V3P2O13 + 3 SiO2 + NaVPO5 -> Na3V4Si3(PO8)3 | 2.5893081 | 0.0699813 |
| **14** | NaVO3 + Na2V3P2O13 + 4 SiO2 -> Na3V4Si4(PO12)2 | 3.222808378 | 0.087102929 |
| **15** | 0.5 Na3V(PO4)2 + 0.5 V2O3 + 0.5 NaV(SiO3)2 + 0.5 Na4P2O7 -> Na4V2Si(PO6)2 | 0.249203056 | 0.011866812 |
| **16** | NaV(SiO3)2 + 0.5 Na3PO4 + 0.25 Na2V3O7 + 0.25 Na4VP2O9 -> Na4V2Si2PO12 | 0.643479102 | 0.030641862 |
| **17** | NaVP2O7 + SiO2 + 3 NaVPO5 -> Na4V4SiP5O24 | 1.225380448 | 0.032246854 |
| **18** | NaVO3 + 3 SiO2 + 3 NaVPO5 -> Na4V4Si3(PO8)3 | 2.686468248 | 0.070696533 |
| **19** | 0.3333 Na4VP2O9 + 0.6667 Na3V3(PO4)4 + SiO2 + 1.667 NaVPO5 -> Na5V4SiP5O24 | 1.015551806 | 0.02603979 |
| **20** | 0.3846 NaV(SiO3)2 + 0.4615 Na4VP2O9 + 2.231 SiO2 + 2.077 NaVPO5 + 0.07692 Na9V14O35 -> Na5V4Si3(PO8)3 | 1.893619671 | 0.048554351 |
| **21** | 0.09091 NaVO3 + 0.6364 Na4VP2O9 + 4 SiO2 + 0.7273 NaVPO5 + 0.1818 Na9V14O35 -> Na5V4Si4(PO12)2 | 2.631381482 | 0.06747132 |
| **22** | 0.5 NaV(SiO3)2 + 0.6667 Na4VP2O9 + 0.8333 Na3V3(PO4)4 + 0.3333 NaVPO5 -> Na6V4SiP5O24 | 0.685964564 | 0.017149114 |
| **23** | 1.192 NaV(SiO3)2 + 0.7308 Na4VP2O9 + 0.6154 SiO2 + 1.538 NaVPO5 + 0.03846 Na9V14O35 -> Na6V4Si3(PO8)3 | 1.647532539 | 0.041188313 |
| **24** | 1.5 Na3V(PO4)2 + 0.3333 V2O3 + 0.5 NaV(SiO3)2 + 0.6667 Na3V2(PO4)3 -> Na7V4SiP5O24 | 0.325494638 | 0.007938894 |
| **25** | 0.5 Na3V(PO4)2 + NaV(SiO3)2 + 0.25 V3O5 + 0.75 Na4VP2O9 + 0.5 Na3V2(PO4)3 -> Na7V4Si2(PO6)4 | 1.005624921 | 0.024527437 |
| **26** | 1.5 NaV(SiO3)2 + 0.25 V3O5 + 1.25 Na4VP2O9 + 0.5 NaVPO5 -> Na7V4Si3(PO8)3 | 1.338450674 | 0.032645138 |

| | | | |
|---|---|---|---|
| **27** | NaVO3 + 2 NaV(SiO3)2 + Na4VP2O9 -> Na7V4Si4(PO12)2 | 1.800793205 | 0.043921785 |
| **28** | 2.303 Na3V(PO4)2 + 0.5141 V2O3 + 0.5 NaV(SiO3)2 + 0.1479 Na4P2O7 + 0.01408 V12P7 -> Na8V4SiP5O24 | 0.574560675 | 0.013680016 |
| **29** | 0.75 V2O3 + 1.5 NaV(SiO3)2 + 0.5 Na3PO4 + 0.25 Na4P2O7 + Na4VP2O9 -> Na8V4Si3(PO8)3 | 1.112470668 | 0.026487397 |

**Table S2** DFT computed reaction energies and corresponding dissociation products of $Na_xV_2P_i(S)_{3-i}O_{12}$.

| | **Reaction** | **Energy (eV/atom)** | **$E^{hull}$ ( eV/atom)** |
|---|---|---|---|
| **0** | VO2 + VPO4 + 2 SO3 -> V2P(SO6)2 | 0.9703326714200100 | 0.05707839243647770 |
| **1** | VPO5 + VPO4 + SO3 -> V2P2SO12 | 0.32226383945993600 | 0.018956696438830400 |
| **2** | SO2 + 3 VO2 + VPO4 + 4 SO3 -> V4PS5O24 | 1.522129259869730 | 0.044768507643246000 |
| **3** | VPO5 + VO2 + 2 VPO4 + 3 SO3 -> V4P3(SO8)3 | 1.297154085880100 | 0.038151590761185800 |
| **4** | 2 VPO5 + VP2O7 + VPO4 + SO3 -> V4P5SO24 | 0.6156082469599940 | 0.018106124910600500 |
| **5** | 0.5 SO2 + VO2 + 0.5 Na2SO4 + SO3 -> NaV(SO4)2 | 0.13082850922499700 | 0.010902375768755400 |
| **6** | 1.5 SO2 + 2 VO2 + 0.5 Na2SO4 + SO3 -> NaV2(SO4)3 | 0.7494697362551220 | 0.041637207569722 |
| **7** | 5 SO2 + 8 VO2 + Na2SO4 + 6 SO3 -> NaV4(SO4)6 + NaV4(SO4)6 | 2.433074989409360 | 0.03475821413442850 |
| **8** | 5 SO2 + 8 VO2 + Na2SO4 + 6 SO3 -> NaV4(SO4)6 + NaV4(SO4)6 | 2.433074989409360 | 0.034760931277285900 |
| **9** | VPO5 + NaV2(PO4)3 + VP2O7 -> NaV4(PO4)6 | 0.3384825025007100 | 0.009670928642879770 |
| **10** | VO2 + Na2SO4 + SO3 -> Na2VS2O9 | 0.4317387319600240 | 0.030838480854288100 |
| **11** | 2 NaPO3 + 2 NaVPO5 -> Na2V(PO4)2 + Na2V(PO4)2 | 0.21251188333326400 | 0.04801199955129400 |
| **12** | 2 NaPO3 + 2 NaVPO5 -> Na2V(PO4)2 + Na2V(PO4)2 | 0.21251188333326400 | 0.008173533974370710 |
| **13** | 2 SO2 + 2 VO2 + Na2SO4 -> Na2V2(SO4)3 | 1.5459732640600200 | 0.08136701389789370 |
| **14** | NaVPO5 + NaVP2O7 -> Na2V2(PO4)3 | 0.25876956250004900 | 0.01361945065788110 |
| **15** | 2 NaVS2 + 0.5 Na2SO4 + 1.5 Na2S -> Na3VS3O + Na3VS3O | 0.32046823000001700 | 0.0201839790624998 |
| **16** | 2 NaVS2 + 0.5 Na2SO4 + 1.5 Na2S -> Na3VS3O + Na3VS3O | 0.32046823000001700 | 0.020029264375001100 |
| **17** | 0.5 SO2 + VO2 + 1.5 Na2SO4 + SO3 -> Na3V(SO4)3 | 0.12872882922501100 | 0.006775201538163250 |
| **18** | 3.5 SO2 + 4 VO2 + 1.5 Na2SO4 + SO3 -> Na3V4(SO4)6 | 2.353280560314890 | 0.06360217730581220 |
| **19** | NaV2(PO4)3 + NaVPO5 + NaVP2O7 -> Na3V4(PO4)6 | 0.3697876924999260 | 0.009994261959458410 |
| **20** | VO2 + 2 Na2SO4 + SO3 -> Na4VS3O13 | 0.31149888696003800 | 0.0148332803314295 |

| | | | |
|---|---|---|---|
| **21** | 0.1481 V2O3 + 1.111 Na3V(PO4)2 + 0.03704 V4P3 + 0.2222 Na3V2(PO4)3 -> Na4V2(PO4)3 | 0.1546666062963030 | 0.007365076490314590 |
| **22** | 0.2308 Na7V4P9O32 + NaVPO5 + 0.6923 Na3V3(PO4)4 + 0.07692 Na4P2O7 -> Na5V4(PO4)6 | 0.3404983509614680 | 0.008730726947704600 |
| **23** | 0.1481 V2O3 + 1.111 Na3V(PO4)2 + 0.03704 V4P3 + 1.222 Na3V2(PO4)3 -> Na7V4(PO4)6 | 0.10553895129629600 | 0.002574120763346070 |

## S4 Energy Density of Hypothetical Compounds

**Figure S4** shows the energy density obtained from the predicted voltages and the theoretical gravimetric capacities. While the average voltages are calculated across the extent of Na (de)intercalation ($x \geq 1.0$) possible (in accordance with physically accessible V oxidation states, see **Figure 2** manuscript), the capacities are referenced to the maximum Na content that is feasible for each compound. For example, the gravimetric capacity for $Na_xVP_1S_2$ is computed across the $1 \leq x \leq 3$ range, and referenced to the molar mass of $Na_3VP_1S_2$. The average voltage in the same Na concentration range is used to get the energy density. Contours corresponding to the theoretical energy densities (product of average voltages and gravimetric capacities) of 300-700 Wh/kg are marked as dashed lines to compare different NaSICONs in **Figure S4**.

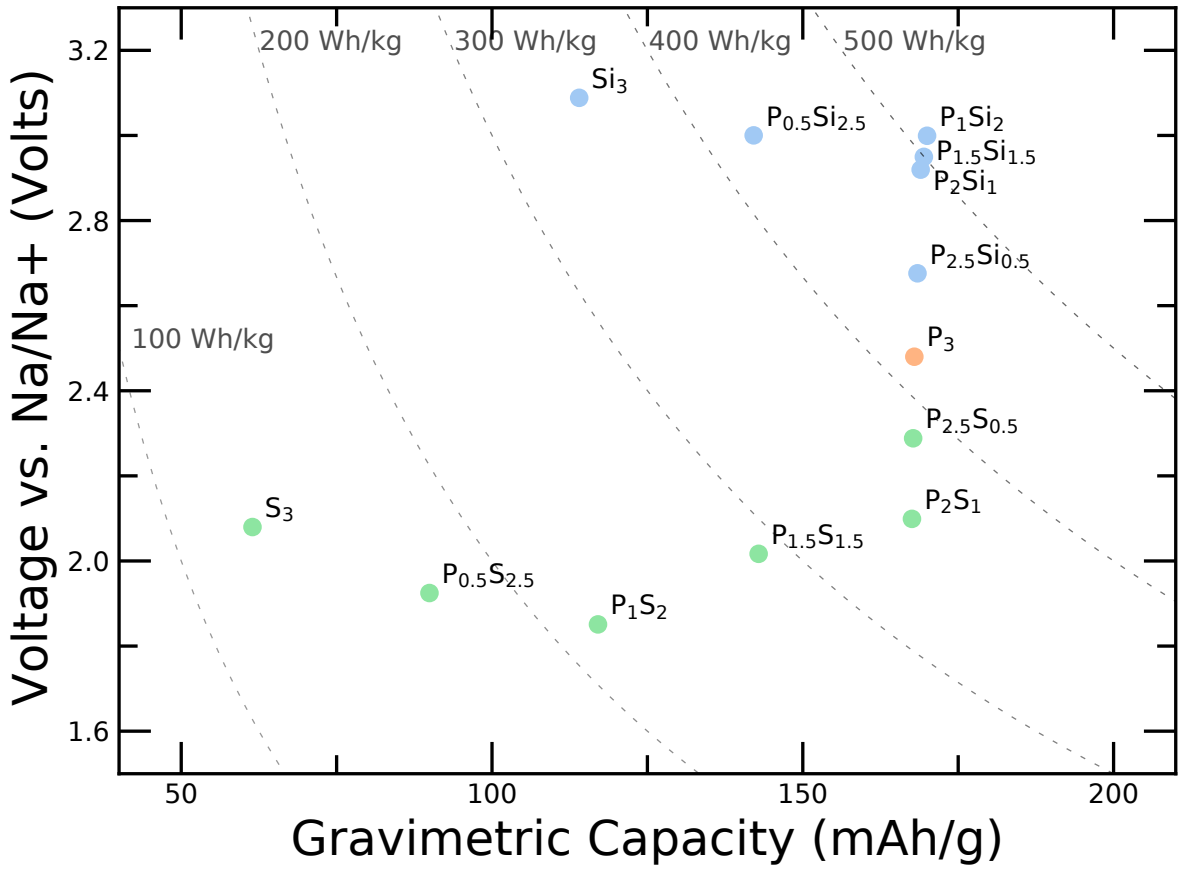


**Figure S4** Correlation of computed average voltages($x \geq 1.0$) of $Na_xVP_{3-i}(Si/S)_i$ NaSICONs and theoretical gravimetric capacities for $Na^+$ deintercalation within the feasible Na concentration range, with $x \geq 1.0$. The upper limits of x for capacity calculation of each computed composition are fixed with respect to the physically accessible V oxidation states (**Figure 2**). Contour lines indicate the energy density.