Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Support information: Two-dimensional GeP_3 as a High Capacity Electrode Material for Li-ion Battery

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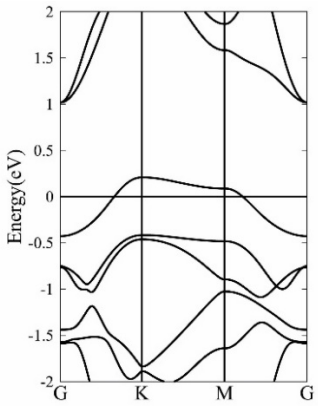

Figure s1. Calculated band structure of 2D $Ge_8P_{24}Li$ from PBE method.

To estimate the interaction between the Li layer and the GeP_3 monolayer, we calculate the average adsorption energy in each layer (E_{ave}), using the following expression:

For the first layer, there are 16 Li atoms, so the binding energy for the first layer is -1.01ev, which is calculated from the equation:

$$E_{ave} = \frac{E_{Ge_8P_{24}Li_{16}} - E_{Ge_8P_{24}} - 16*E_{Li}}{16} \qquad \text{(s1)}$$

E_{Li} is the cohesive energy of the bulk metal (Li); $E_{Ge_8P_{24}}$ and $E_{Ge_8P_{24}Li_{16}}$ are the total energies of GeP_3 2 x 2 supercell before and after Li adsorption.

For the second layer, there are 8 Li atoms adsorbed on the surface, with a binding energy -0.225 eV, which is calculated from the equation:

$$E_{ave} = \frac{E_{Ge_8P_{24}Li_{24}} - E_{Ge_8P_{24}Li_{16}} - 8*E_{Li}}{8} \qquad \text{(s2)}$$

For the third layer, there are also 8 Li atoms adsorbed on the surface, with a binding energy -0.112 eV, which is calculated from the equation:

$$E_{ave} = \frac{E_{Ge_8P_{24}Li_{32}} - E_{Ge_8P_{24}Li_{24}} - 8*E_{Li}}{8} \qquad \text{(s3)}$$

Adsorption coordination

In 2 x 2 supercell monolayer GeP_3, there are 4 Ge1 sites, 4 Ge2 sites, 12 P1 sites, and 12 P2 sites. The Li adsorption sites are given in Figure s1.

The 1st layer can accommodate up to 8 Li atoms each side, 4 above Ge 2, and another 4 above P1 site.

The 1st layer: 4 Li atom above Ge2 position with a adsorption distance 3.117Å: Ge2-1: (3.81, 0.68, 12.25), Ge2-2: (3.81, 7.54, 12.25), Ge2-3: (9.75, -2.74, 12.25), Ge2-4 (9.75, 4.12, 12.25)

The 1st layer: 4 Li atom above P1 position with a adsorption distance 2.888 Å: P1-1: (3.82, 4.10, 12.62), P1-2 (3.82, 10.97, 12.62), P1-3 (9.75, 0.68, 12.62), P1-4 (9.75, 7.54, 12.62)

The 2nd layer: 4 Li atom above P1 position with adsorption distance 4.648 Å: P1-5: (0.79, 9.26, 12.82), P1-6: (0.79, 2.40, 12.82), P1-7: (6.72, -1.02, 12.82), P1-8: (6.72, 5.84, 12.82)

The 3rd layer: 4 Li atom above P2 position with a adsorption distance 4.916 Å: P2-1: (2.83, 5.80, 13.64), P2-2: (2.83, -1.06, 13.64), P2-3: (8.77, 2.38, 13.64), P2-4: (8.77, -4.48, 13.64)

These different adsorption sites guarantee that Li atoms can bind tightly on the GeP_3 monolayer without forming cluster. Besides, the z coordinate difference between 1st and 2nd layer (12.25, 12.62, and 12.82) indicates the slight structure deformation of GeP_3 monolayer.

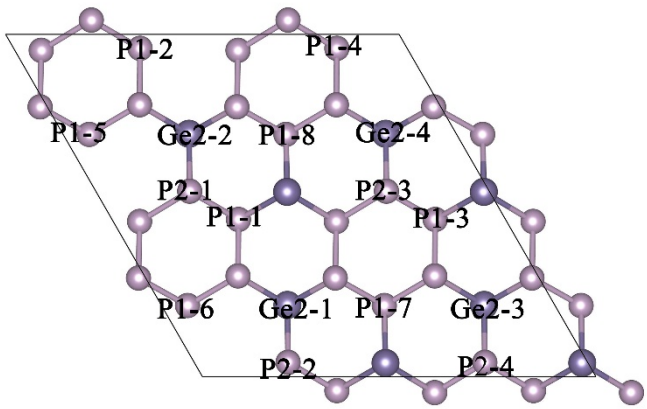

Figure s2, the 1st, 2nd and 3rd Li adsorption sites.