Supplemental Information

Strong influence of strain gradient on lithium diffusion: A theoretical study

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Supplementary Note 1

The Li diffusion pathway and energy barrier in solids are determined by the potential energy profile in the lattice, which is related to the crystalline structure and the atomic arrangements.[1] Fig. S1a and S1b show the energy profiles of pristine and 5 % mid-strain gradient cases, respectively; the calculated paths are from site A to site B based on 4 × 2 × 1 supercell. The activation energy of 0.29 eV (E_{b1}) for pristine BLG is the barrier to enter the site B, which is the energy required to drive the adjacent site transition for diffusion Li atom. Due to the lattice periodic symmetry, the barrier of path from site B to site A is the same as that of from site A to site B. For the strain gradient case, the Li potential energy of site B is smaller than that of site A, so the energy barriers E_{b2} for site A to site B (positive strain gradient case) and E_{b3} for site B to site A (negative strain gradient case) are different; both barriers are also the energy required to drive the adjacent site transition for diffusion Li atom.

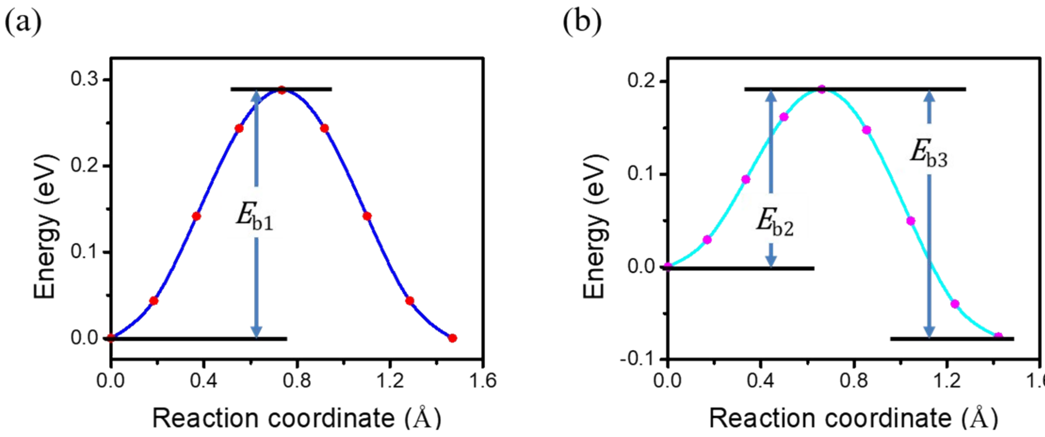

Fig. S1. The energy profiles of (a) pristine and (b) 5 % mid-strain gradient BLG.

Supplementary Note 2

We discuss how the concentrated compressive stress enhance the conductivity of LIBs with the flexo-diffusion effect. The compressive stress is applicable in the LIBs application, but is harmful based on the uniform strain modulation. However, with the flexo-diffusion effect, concentrated compressive stress inducing positive strain gradient could also be useful for enhancing conductivity. We consider that Li diffuses in the BLG electrode (its length is L) with strain gradient, and applying concentrated pressure at the left end ($x = 0$). The out-of-plane strain is $-\varepsilon$ ($\varepsilon > 0$) at $x = 0$, and the magnitude of strain gradient is constant. The strain field is given by

$$\varepsilon(x) = (\frac{x}{L} - 1)\varepsilon \tag{1}$$

For studying the diffusion properties along strain gradient direction at electrode scale, a long-range average equivalent A_2 should be used instead. Substituting Supplementary equation (1) into

$$E_B = A_0 + A_1\varepsilon + A_2\frac{d\varepsilon}{dx} \tag{2}$$

the energy barrier can be rewritten as

$$E_B(x) = A_0 + A_1(\frac{x}{L} - 1)\varepsilon + A_2\frac{\varepsilon}{L} \tag{3}$$

We define the equivalent diffusion coefficient by

$$\bar{D} = \frac{1}{L}\int_0^L D dx \tag{4}$$

For the pristine BLG, the equivalent diffusion coefficient can be calculated by

$$\overline{D} = \frac{1}{L}\int_0^L D_0 e^{-kA_0} dx = D_0 e^{-kA_0} \tag{5}$$

where $k = 1/k_B T$. For the case of positive strain gradient induced by concentrated pressure, the equivalent diffusion coefficient can be calculated by

$$\overline{D} = \frac{1}{L}\int_0^L D_0 e^{-k\left[A_0 + A_1\left(\frac{x}{L} - 1\right)\varepsilon + A_2\frac{\varepsilon}{L}\right]} dx = \frac{D_0}{kA_1\varepsilon} e^{-k\left(A_0 - A_1\varepsilon + A_2\frac{\varepsilon}{L}\right)}\left(1 - e^{-kA_1\varepsilon}\right) \tag{6}$$

For enhancing Li conductivity in BLG through applying compressive stress, the results in Supplementary equation (6) should be greater than that of Supplementary equation (5), and then we can obtain the criterion

$$(1 - e^{kA_1\varepsilon}) \cdot e^{-kA_2\frac{\varepsilon}{L}} > -kA_1\varepsilon \tag{7}$$

The criterion indicates a competition between the applied concentrated compressive strain and its inducing strain gradient. An applied concentrated compressive strain needs inducing a suitable positive strain gradient, which depends on the electrode size *L*. When Supplementary equation (7) is satisfied, the enhancement of positive strain gradient overcomes the reduction effect of compressive strain and hence improve the conductivity of LIBs.

Supplementary references

1 Ning, F.; Li, S.; Xu, B.; Ouyang, C. Strain tuned Li diffusion in $LiCoO_2$ material for Li ion batteries: A first principles study. *Solid State Ionics* **2014**, 263, 46-48.