Supporting Information

Two-Fold Anisotropy Governs Morphological Evolution and Stress Generation in Sodiated Black Phosphorous for Sodium Ion Batteries

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In our finite-strain chemo-mechanical model, the elastic stretch rate induced by sodiation obeys Hooke's law with the stiffness tensor, C_{ijkl}. For black phosphorous, which is an orthotropic material, its stiffness tensor consists of 9 independent material constants. As the sodium concentration increases, the material changes from orthotropic to isotropic. Therefore, at the fully sodiated stage, the stiffness tensor contains only 2 independent material constants. Here, we choose Young's modulus, $E = 35\text{GPa}$, and Poisson's ratio, $\nu = 0.3$, as the two independent constants. Correspondingly, the stiffness tensor at the fully sodiated stage can be derived by the equations below.

$$C_{1111} = C_{2222} = C_{3333} = E(1-\nu)/[(1+\nu)(1-2\nu)] \tag{1}$$

$$C_{1122} = C_{2233} = C_{1133} = E\nu/[(1+\nu)(1-2\nu)] \tag{2}$$

$$C_{1212} = C_{2323} = C_{1313} = E/(1+\nu) \tag{3}$$

The parameters of the stiffness tensor are listed in Table S1.

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Table S1. Stiffness tensor at unsodiated (BP) and fully sodiated (N_3P) stages (in GPa).[1]

Parameter	BP	N_3P
C_{1111}	188.06	47.12
C_{2222}	57.30	47.12
C_{3333}	35.26	47.12
C_{1122}	34.04	20.19
C_{2233}	1.72	20.19
C_{1133}	-2.90	20.19
C_{1212}	55.02	26.92
C_{2323}	8.92	26.92
C_{1313}	18.30	26.92

In the first step, sodiation proceeds with a diffusive interphase and forms the $Na_{0.25}P$ phase. Compared to the terminal phase Na_3P, the amount of sodium atoms inserted into phosphorous in the first step is small, and the induced volume expansion and mechanical stress are expected to be low. As shown in Fig. S1 and S2, the calculated hydrostatic stress and the first principal stress are both much less than the yield strength. We also note that during the first-step sodiation the stresses become progressively low as sodiation proceeds and the residual stress in the bulk is rather small at the end of the first step. For these reasons, we decided to focus our discussions on the second step.

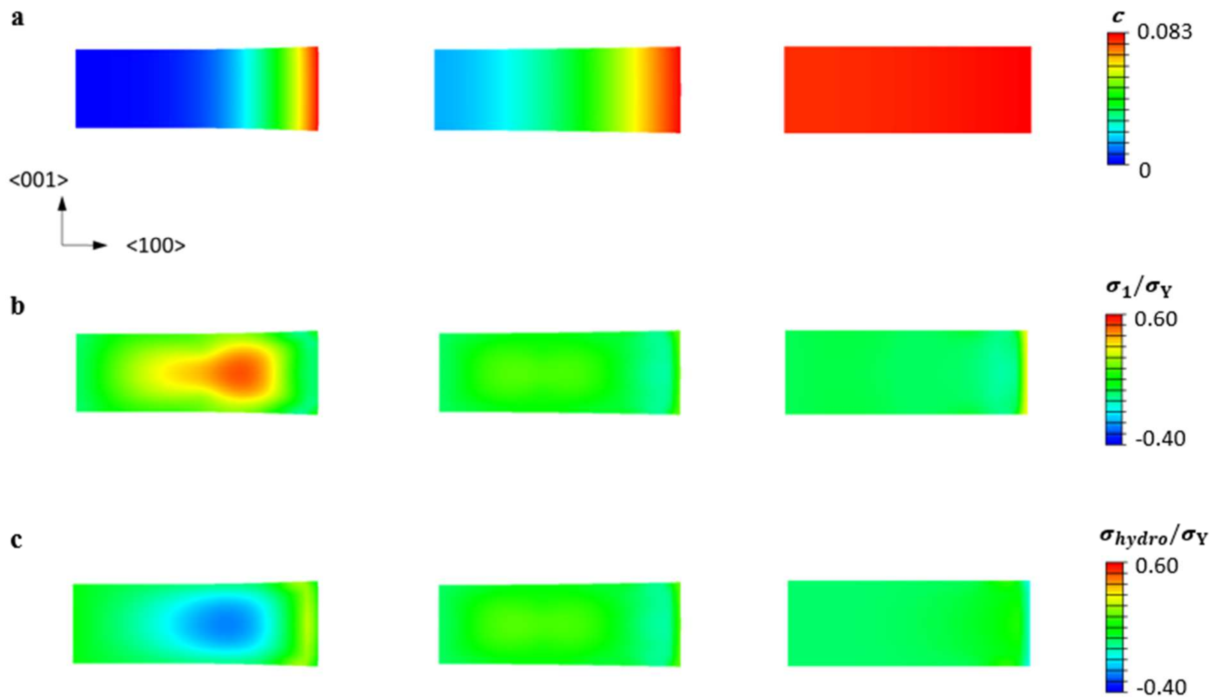

Figure S1. (a) Sodium concentration profile, (b) the first principal stress, and (c) the hydrostatic stress distributions in the first step of sodiation with sodium source on the {100} surface.

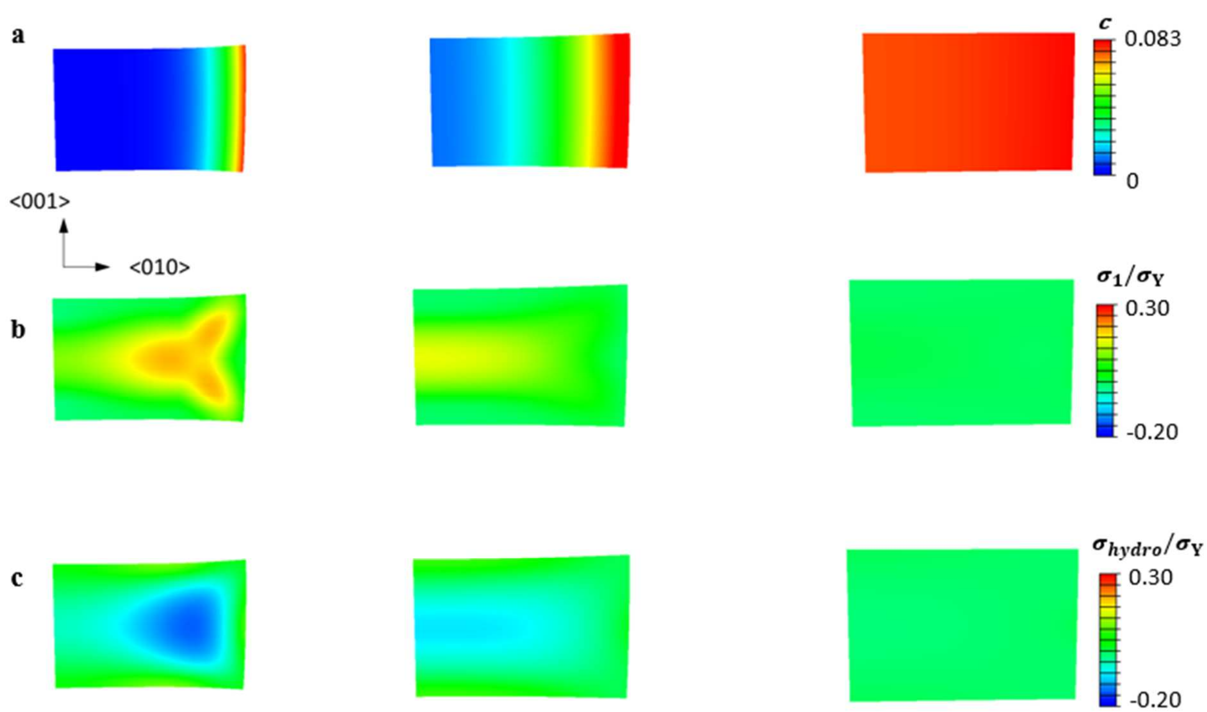

Figure S2. (a) Sodium concentration profile, (b) the first principal stress, and (c) the hydrostatic stress distributions in the first step of sodiation with sodium source on the {010} surface.

References

1. Appalakondaiah, S.; Vaitheeswaran, G.; Lebegue, S.; Christensen, N. E.; Svane, A. *Phys. Rev. B* **2012,** 86, 035105.