Computational study of the surface stability of Li_3AlN_2 and AlN_2 as cathode materials for lithium ion batteries

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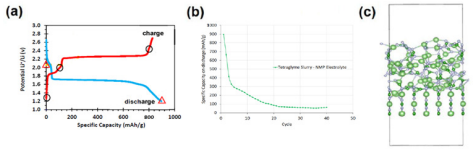
Background

Li_3BN_2/$LiBN_2$ and Li_3AlN_2/AlN_2 have recently been identified as promising high capacity cathode materials. Despite experimental data showing unprecedented high capacities, the capacities rapidly decreases upon multiple charge/discharge cycles.



(a) the charge/discharge curve of $LiBN_2$ showing a capacity of 890 mAh/g, (b) the observed capacity as a function of number of cycles, and (c) surface distortion predicted from AIMD simulations

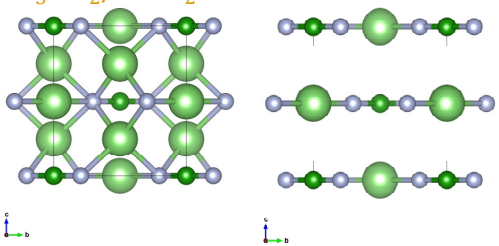
One possible explanation for this happening is structural distortion on the surfaces of these crystals. This work aims to analyze various low-index surfaces to determine the role of surface distortion on the electrochemical instability that leads to capacity fading.

Methodology

b-initio Vienna ackage imulation

The calculations were performed within the density functional theory (DFT) using a plane-wave basis set. The exchange correlation potential is described by a generalized gradient approximation with the Perdew-Burke-Ernzerhof parametrization. The projector-augmented wave method was applied as implemented in the Vienna ab initio simulation package (VASP). The MedeA software was used to generate various crystal structure and surface geometry. Ab initio molecular dynamics was also performance to generate the pair distribution functions of the equilibrium structure.

Li_3BN_2/$LiBN_2$



Views along the a-axes of crystals Li_3BN_2 (left) and $LiBN_2$ (right).

Lattice Constants (Å)

	Li_3BN_2	$LiBN_2$
a=b	4.651	4.571
c	5.171	5.428
Volume	111.869	113.401

Li_3BN_2 and $LiBN_2$ were analyzed in a series of steps, the first being a series of relaxations to determine the minimal energy structure of the crystal as well as a determination of the lattice constant.

Calculated Energies (eV)

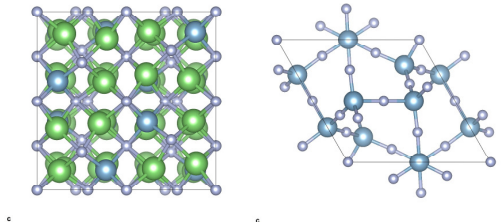
Li_3BN_2 (per molecule)	-28.014343
$LiBN_2$ (per molecule)	-19.272123
Li (per atom)	-0.7363837

$$2Li + LiBN_2 \rightarrow Li_3BN_2$$

$$\Delta E = -7.269 \text{ eV}$$

$$V = 3.635 \text{ eV}$$

Li_3AlN_2/AlN_2



Views along the a-axes of crystals Li_3AlN_2 (left) and AlN_2 (right).

Lattice Constants (Å)

	Li_3AlN_2	AlN_2
a=b=c	9.468	7.981
Volume	848.713	508.286

Li_3AlN_2 and AlN_2 were analyzed in the same series of steps as for the analysis of Li_3BN_2 and $LiBN_2$. The structures shown are the results of these calculations and are being used for all subsequent calculations.

Calculated Energies (eV)

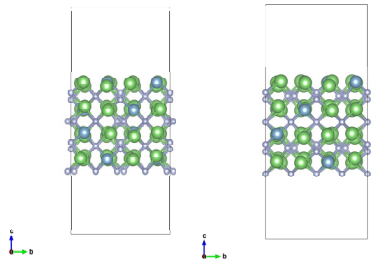
Li_3AlN_2 (per molecule)	-25.59896
AlN_2 (per molecule)	-14.26123
Li (per atom)	-0.7363837

$$3Li + AlN_2 \rightarrow Li_3AlN_2$$

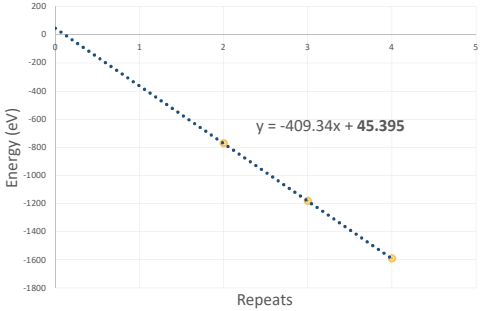
$$\Delta E = -9.129 \text{ eV}$$

$$V = 3.04 \text{ eV}$$

Surface Analysis

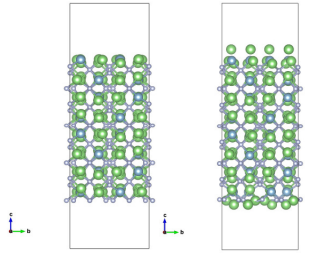


Views along the a-axes of Li_3AlN_2 – surfaces 100 (left) and 010 (right).



$E_{0,\,100}$ = 45.395 eV E_{100} = 0.0422 eV/Å^2 = **0.676 J/m^2**

Evidence of surface distortion can be seen in the structure of surface 100. Coatings of Carbon and Aluminum will be tested to determine their usefulness in preventing this following more calculations involving various other low-index surfaces.



Views along the a-axes of Li_3AlN_2, surface 100 with two repeats before (left) and after (right) calculations.

Acknowledgements

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