Computational study of the surface stability of Li$_3$AlN$_2$ and AlN$_2$ as cathode materials for lithium ion batteries

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**BACKGROUND**

Li$_3$BN$_2$/LiBN$_2$ and Li$_3$AlN$_2$/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.

Views along the a-axes of crystals Li$_3$BN$_2$ (left) and LiBN$_2$ (right).

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**METHODOLOGY**

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 Medeek software was used to generate various crystal structure and surface geometry. Ab initio molecular dynamics was also performed to generate the pair distribution functions of the equilibrium structure.

Lattice Constants (Å)

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<tr>
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<th>Li$_3$BN$_2$</th>
<th>LiBN$_2$</th>
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<tbody>
<tr>
<td>a=b</td>
<td>4.651</td>
<td>4.571</td>
</tr>
<tr>
<td>c</td>
<td>5.171</td>
<td>5.428</td>
</tr>
<tr>
<td>Volume</td>
<td>111.869</td>
<td>113.401</td>
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</tbody>
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Calculated Energies (eV)

- Li$_3$BN$_2$: -28.014343
- LiBN$_2$: -19.272123
- Li (per atom): -0.7363837

Li$_3$BN$_2$ 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.

2Li + LiBN$_2$ → Li$_3$BN$_2$

$\Delta E = -7.269$ eV

$V = 3.635$ eV

(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.

**SURFACE ANALYSIS**

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.

Calculated Energies (eV)

- Li$_3$AlN$_2$: -25.59896
- AlN$_2$: -14.26123
- Li (per atom): -0.7363837

Li$_3$AlN$_2$ and AlN$_2$ were analyzed in the same series of steps as for the analysis of Li$_3$BN$_2$ and LiBN$_2$. The structures shown are the results of these calculations and are being used for all subsequent calculations.

3Li + AlN$_2$ → Li$_3$AlN$_2$

$\Delta E = -9.129$ eV

$V = 3.04$ eV

**ACKNOWLEDGEMENTS**

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