

First principles modeling of the interface between a solid state lithium thiophosphate electrolyte and a lithium metal anode

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Recently, there has been progress in improving the conductivity and stability of solid electrolytes such as Li_3PS_4 . [1] We report the results of first principles computer modeling studies of ideal Li_3PS_4 electrolyte interfaces with metallic Li anodes.

For a variety of interface configurations, computer modeling studies show that Li_3PS_4 surfaces are structurally and chemically altered by the presence of Li metal. On the other hand, experiments have shown [1] that an electrochemical cell of $\text{Li}/\text{Li}_3\text{PS}_4/\text{Li}$ can be cycled many times. One possible explanation of the apparent stability of the Li_3PS_4 electrolyte/Li metal interface, is that a stable thin buffer layer is formed during the first few cycles. In order to computationally explore this possibility, we modeled a “thin film” buffer layer of Li_2S on the surface of the electrolyte. Using first principles techniques described in previous work, [2] stable electrolyte-buffer layer configurations were found. Results for the idealized configurations indicate that a thin film of Li_2S can provide a protective buffer layer to stabilize the interface between the Li_3PS_4 electrolytes and Li metal anodes.

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References

- [1] Z. Liu, W. Fu, E. A. Payzant, X. Yu, Z. Wu, N. J. Dudney, J. Kiggans, K. Hong, A. J. Rondinone, and C. Liang, *J. Am. Chem. Soc.* **135**, 975-978 (2013).
[2] N. A. W. Holzwarth, N. D. Lepley, and Y. A. Du, *J. Power Sources* **196**, 6870-6876 (2011).