Probing structural changes in the lithium imide system through anion doping

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The Li-N-H system has been tested previously for its ability in catalysis and energy storage (hydrogen and Li-ion batteries). Recently, lithium imide (Li_2NH) has been proven to be a good candidate as a solid electrolyte[1], but higher conductivity and lower activation energy for Li-ion mobility would greatly improve its practical applicability.

This work utilises the compositional flexibility of the antifluorite Li_2NH structure to a range of different anions to explore these aims. Through two different doping regimes, via solid-state synthesis, lithium bromide (Br^-) and chloride (Cl^-) were used in an attempt to lower the activation energy of Li-ion mobility, while lithium nitride (N^{3-}) is used to "stuff" extra charge carriers into the structure. X-ray diffraction was used to evaluate the structural impact of these dopants, alongside electrochemical testing to probe the conductivity and electrochemical stability.

Nitride doping resulted in products with the general formula $Li_{2+x}NH_{1-x}$ (where $0<x<0.22$). These excess Li^+ ions were refined in the octahedral interstitial sites in the Li_2NH structure, with evidence for a disruption of the *Fd3̄m* supercell is shown in **Figure 1a and 1b**, suggesting the increase of N^{3-} anions in the NH^{2-} site disrupts the long-range N-H bond ordering, which is at the basis of this *2ax2ax2a* antifluorite supercell. The increased number of charge carriers appears to increase the ionic conductivity of these materials, with results indicating that a saturation of excess Li^+ is reached at x = 0.14, whereby the conductivity significantly decreases, shown in **Figure 1c**.

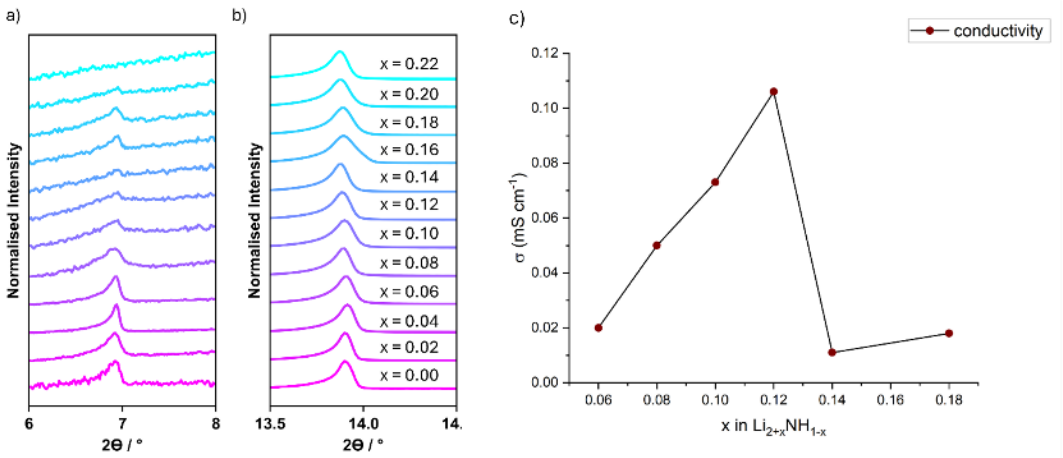


Figure 1a) *indicating the decrease of the Fd-3m peak at ~6.9°* ***b)*** *shows the increasing broadness of the Fm-3m peak at ~13.8°****c)*** *shows the trend in conductivity seen with these materials*

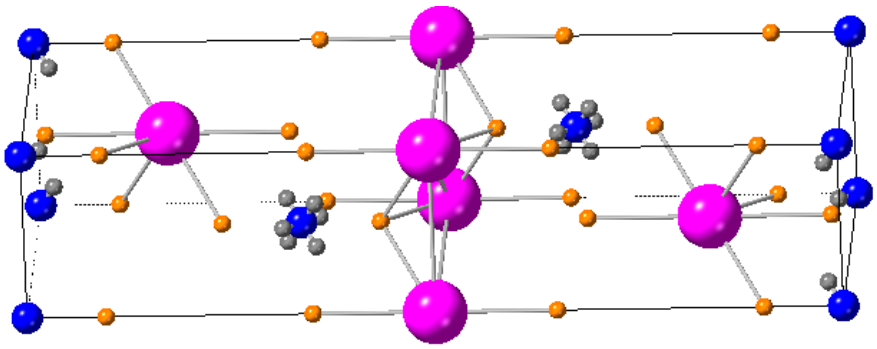


Figure 2 *R3̄m $Li_3(NH)Br$ crystal structure, where hydrogen is depicted in grey, lithium in orange, nitrogen in blue and bromine in pink.*

Chloride and bromide doping resulted in products with the general formula $Li_{2-x}(NH)_{1-x}(Cl/Br)_x$ forming a disordered antifluorite structure. For chloride this was the only phase observed ($0.1<x<0.5$), while bromide doping at higher levels revealed a new $Li_3(NH)Br$ phase (*R3̄m* space group, analogus to lithium nitride chlorides[3], shown in **Figure 2**). A a series of double-anion-doped lithium imide samples have also been synthesised.

[1] J. P. Lowen, T. Insinna, T. V. Beatriceveena, M. P. Stockham, B. Dong, S. J. Day, C. P. Grey, E. Kendrick, P. R. Slater, P. A. Slater and J. W. Makepeace, *EES Batteries*, 2025, DOI: 10.1039/D5EB00058K **[2]** P. A. Chater, P. A. Anderson, D. R. Hewett and P. R. Slater, *Faraday Discussions*, 2010, **151**, 271-284. **[3]** V. Landgraf, T. Famprikis, J. de Leeuw, L. J. Bannenberg, S. Ganapathy and M. Wagemaker, *ACS Appl. Energy Mater.* 2023, **6**, 3, 1661–1672