High magnesium mobility in ternary spinel chalcogenides

Pieremanuele Canepa[a,b], Shou-Hang Bo,[a,b] Gopalakrishnan Sai Gautam,[b,a] Tan Shi,[c,a] Yaosen Tian,[c,a] and Gerbrand Ceder[a,c,b]

[a]*Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA*

[b]*Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA*

[c]*Department of Materials Science and Engineering, University of California Berkeley, Berkeley, CA, 94720, USA*

E-mail: ystian@berkeley.edu

Magnesium batteries appear a viable alternative to overcome the energy density limitations faced by current Li-ion technology. The development of a competitive magnesium battery is plagued by the existing notion of poor magnesium mobility in solids [1-4]. Poor Mg transport also curbs the use of solid barrier coatings to protect electrodes from reaction with the liquid electrolyte, or the development of full solid-state magnesium batteries, which would alleviate many of today's problems caused by liquid electrolytes.

In this poster, we show that high Mg^{2+} mobility in solids can be achieved by judicious tuning of crystal structure and chemistry. By combining first-principles calculations, synchrotron X-ray diffraction, electrochemical impedance spectroscopy and solid-state nuclear magnetic resonance, we demonstrate facile Mg^{2+} conduction at room temperature [5]. Experimentally, we demonstrate the discovery of the first generation of crystalline solids, i.e., spinel MgX_2Z_4, with $X = (In, Y, Sc)$ and $Z = (S, Se)$, which possess high Mg^{2+} cation mobility at room temperature. Mg NMR relaxometry and impedance spectroscopy confirm the fast Mg^{2+} motion with a low migration barrier ($\sim 370 \pm 90$ meV). First-principles calculations and ab initio molecular dynamics indicate that several other spinels in this family are likely to also have high Mg mobility, including MgY_2S_4 (~ 360 meV) and MgY_2Se_4 (~ 361–326 meV). Finally, we propose practical design rules to identify fast multivalent-ion solid conductors.

References:

[1] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R Turgeman, Y. Cohen, M. Moshkovich, and E. Levi, *Nature* 407, (2000) 724-727.

[2] P. Canepa, G. S. Gautam, D. C. Hannah, R. Malik, M. Liu, K. G. Gallagher, K. A. Persson, and G. Ceder, *Chem. Rev.* 117, (2017) 4287–4341.

[3] Z. Rong, R. Malik, P. Canepa, G. S. Gautam, M. Liu, A. Jain, K. Persson, and G. Ceder, *Chem. Mater.* 27, (2015) 6016–6021.

[4] M. Liu, Z. Rong, R. Malik, P. Canepa, A. Jain, G. Ceder, and K. Persson, *Energy Environ. Sci.* 8, (2015) 964–974.

[5] P. Canepa, S.-H. Bo, G. S. Gautam, B. Key, W. D. Richards, T. Shi, Y. Tian, J. Li, and G. Ceder, *Nat. Comm.* 8, (2017) 1759.