Thermodynamics and Ion Transport of Multivalent Cathode Materials

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Abstract: Multi-valent (MV) batteries that replace Li^+ ions with inexpensive MV cations, including Mg^{2+}, Zn^{2+} and Ca^{2+} represent a promising approach to meet the high energy density requirements of the next generation of electrical devices.[1] Perhaps the most pressing challenge in achieving high energy density MV-ion systems is to develop suitable cathode materials and conductors with a significant voltage and high MV-ion transport.[1-2] To date, there have been limited examples demonstrating the feasibility of rechargeable MV batteries, and among them, most of the focus has been on Mg technology. From the limited experimental studies performed so far, the feasibility of a battery technology based on MV intercalation is not yet clear. The cathode represents a critical component of this technology. Therefore, it is crucial to assess the feasibility of MV cathodes. I will present a detailed analysis, based on first-principles DFT calculations, of MV intercalation in promising candidates, including the spinel MVB_2X_4 system (with B = transition metal and X the anion) and the polymorphs of the layered vanadium pentoxide (V_2O_5).[1-7] I will demonstrate that computational materials science is a powerful tool to pave the successful development and optimization of new materials for energy dense MV batteries.

References:

[1] P. Canepa, G. S. Gautam, D. C. Hannah, R. Malik, M. Liu, K. G. Gallagher, K. Persson and G. Ceder, Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges, *Chem. Rev.*, 2017, 117 (5), 4287.

[2] P. Canepa, S.-H. Bo, G. S. Gautam, B. Key, W. D. Richards, T. Shi, Y. Tian, Y. Wang, J. Li and G. Ceder, High magnesium mobility in ternary spinel chalcogenides, *Nature Communications,* (2017) 8, 1759.

[3] G. S. Gautam, P. Canepa, R. Malik, M. Liu, K. Persson and G. Ceder, First-principles evaluation of multi-valent cation insertion into orthorhombic V_2O_5

[4] Z. Rong, R. Malik, P. Canepa, G. S. Gautam, M. Liu, A. Jain, K. Persson and G. Ceder, Materials Design Rules for Multi-Valent Ion Mobility in Intercalation Structures, *Chem. Mat.* 2015, 27, 6016. **[5]** M. Liu, Z. Rong, R. Malik, P. Canepa, A. Jain, G. Ceder and K. Persson, Spinel compounds as multivalent battery cathodes: a systematic evaluation based on *ab initio* calculations, *Energy Environ. Sci.* 2015 8, 964.

[6] G. S. Gautam, P. Canepa, A. Abdellahi, A. Urban, R. Malik and G. Ceder, Intercalation phase diagram of Mg in V_2O_5 from first principles, *Chem. Mat.* 2015, 27, 3733.

[7] M. Liu, A. Jain, Z. Rong, X. Qu, P. Canepa, R. Malik, K. Persson and G. Ceder, Evaluation of sulfur spinel compounds for multivalent battery cathode applications, *Energy Environ. Sci.*, 2016, 9,3201.