Thermodynamic pathway yields stable nano-$LiMn_2O_4$ for Co-free Li-ion battery cathode

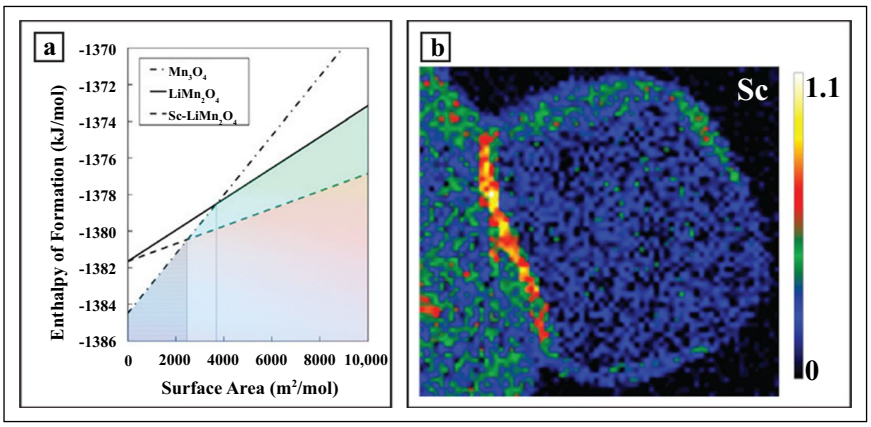
Cobalt is the most common element used in commercial lithium-ion (Li-ion) battery systems. This is draining the limited Co resources and its price has skyrocketed. Researchers are consequently seeking reliable Co-free cathode chemistries for Li-ion batteries. Lithium manganese oxide (LMO), a Co-free cathode, could be a promising replacement for lowering the cost of Li-ion batteries, owing to the abundance of manganese and cost-effective processing; however, its poor performance—particularly at elevated temperatures—limits its practical applications.

Researchers at the University of California, Davis, in the Nanoceramics Thermochemistry Laboratory led by Ricardo Castro, are trying to understand the problems associated with thermodynamic nature interfacial reactions and picture a new perspective. In their article, published in a recent issue of *Chemistry of Materials* (https://pubs.acs.org/doi/10.1021/acs.chemmater.0c04305), Castro's research team explored the issues that limit the performance of LMO at the nanoscale. Many properties of the material—such as reactivity, phase transitions, and coarsening—depend on the interfacial characteristics at the nanoscale. "When you go to the nanoscale, a huge fraction of your atoms are located at interfaces, so you might expect that interfacial energies would affect the behavior," Castro says.

Owing to their previous experience of studying zirconia's phase diagram at the nanoscale, Castro says, "contrary to what a lot of people think, that the nanoworld is kinetically driven, our work proves otherwise. Our work proves that if you know thermodynamics, you can actually not only predict but also understand and control phase transformations at the nanoscale." Experimental studies of the interfacial and grain-boundary energies of Li-ion battery cathode materials are very limited, and the available data are mostly restricted to simulation efforts, lacking an experimental benchmark. Castro's team carried out experiments to modulate and lower the surface energy of nanostructured LMOs and improve the cathode stability. Lower surface energy suppresses undesirable side reactions in the cathode and excess grain-boundary energy, which is the driving force of nanoscale crack formation—a critical barrier for high-voltage applications.

Castro's group studied the average surface and grain-boundary energy of fully oxidized spinel LMO nanoparticles using a calorimetry approach, based on the knowledge that the exothermic heat of sintering is correlated to changes in surface and grain-boundary areas and their associated energies. The researchers were able to generate a comprehensive database of the total excess energies in nanocrystalline LMO that may be used as a roadmap for other researchers, especially electrochemists. Furthermore, they have also shown that scandium-doping of the LMO structure would significantly lower the surface energies since Sc atom segregation to grain boundaries changes the distribution of Li^+.

Ali Rashti



(a) Enthalpy of formation of spinel Sc-LMO (lithium manganese oxide) versus LMO and Mn_3O_4 as a function of surface area; (b) scanning transmission electron microscope image of Sc-doped LMO nanoparticles. Credit: *Chemistry of Materials*.