# Non-Equilibrium Crystallization Pathways of Manganese Oxides in Aqueous Solution

## Scientific Achievement

Revealing the metastable energy landscape of Pourbaix diagrams helps to rationalize multistage crystallization pathways of transition-metal oxides from solution.

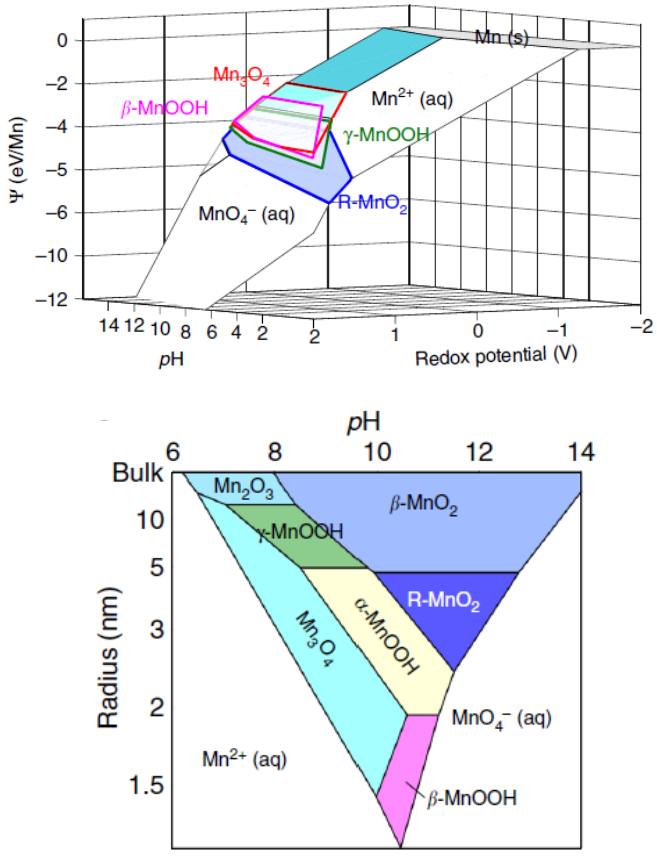
## Significance and Impact

Being able to rationalize which metastable phases form in solution—and why—is crucial toward developing predictive theoretical frameworks for solution synthesis.

## Research Details

- We derived a thermodynamic potential for Pourbaix diagrams, adding a free-energy axis to Pourbaix diagrams. These 3D Pourbaix diagrams reveal the metastable energy landscape of aqueous precipitation.
- By adding surface energies to the Pourbaix potential, we constructed the first nanoscale Pourbaix diagrams, showing the size stabilization of metastable Mn oxide polymorphs.
- We derived a nucleation model to rationalize the multistage crystallization pathways of complex metal oxides from solution.

W. Sun, D. Kitchaev, D. Kramer, G. Ceder, *Nature Communications* **10**(1), 573 (2019).




*(Top): Metastable phases represented on a 3D Pourbaix diagram. (Bottom): Nanoscale Pourbaix diagrams constructed by adding surface energies to the Pourbaix potential.*