Phase Selection in MnO_2 Structures During Aqueous Growth

Scientific Achievement

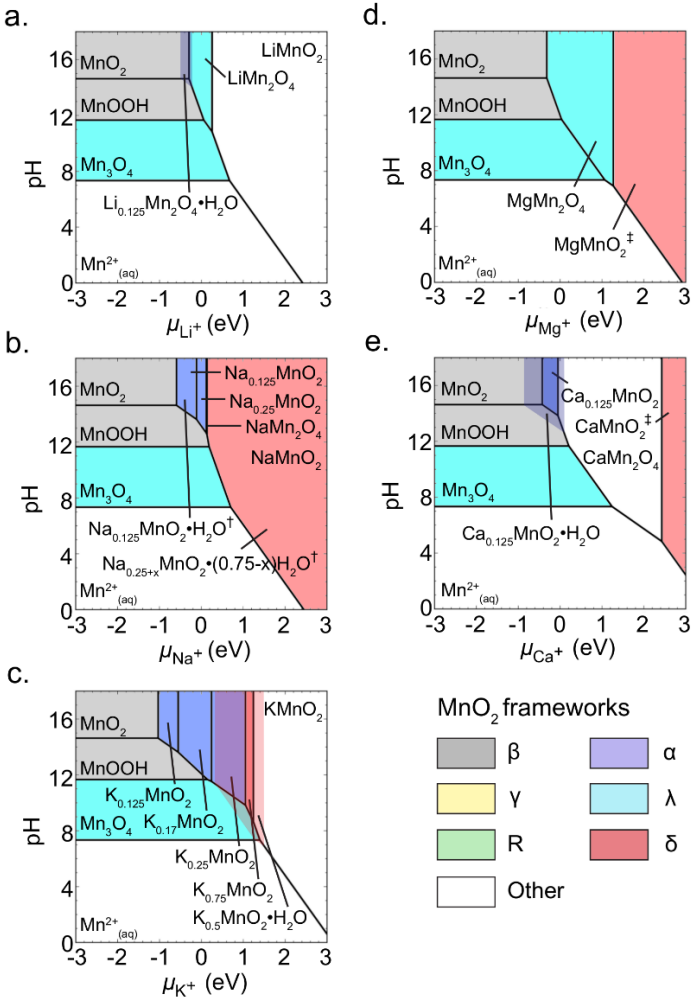
Rationalized the synthesis of all common MnO_2 polymorphs by forming off-stoichiometric intermediates during aqueous synthesis. Derived general rules governing off-stoichiometric polymorph stabilization by alkali ions and hydration applicable to transition metal oxide chemistries.

Significance and Impact

Control of crystal structure in the synthesis of transition metal oxides is critical for achieving high performance in energy storage, catalysis, and optical device applications. Using off-stoichiometry for structure selection ties theory to readily implementable synthetic procedures, moving toward the goal of Synthesis-by-Design.

Research Details

- First-principles modeling of $A_xMnO_2 \cdot yH_2O$ chemistries using new SCAN method previously benchmarked by CNGMD and CCDM collaboration
- Alkali, alkali-earth ions in solution lead to variety of A_xMnO_2 structures, from which "A" can be extracted to obtain common β, α, λ, δ MnO_2 polymorphs
- Metastable proton defects stabilize R, γ phases
- Hydration gives a further handle for structure control



Structure selection in $A_xMnO_2 \cdot yH_2O$ growth intermediates across aqueous solution conditions for A = H, Li, Na, K, Mg, Ca

D.A. Kitchaev, S.T. Dacek, W. Sun, G. Ceder. *J. Am. Chem. Soc.* **139**(7), 2672–2681 (2017).

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