Linking Phase Stability and Oxygen-Vacancy Energetics in High-Entropy Oxide Nanofibers via Machine-Learned Potentials

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High-entropy oxide (HEO) nanofibers are promising architectures for electrochemical energy storage electrodes. They combine high surface area, compositional tunability, and multi-cation redox activity. However, the same compositional flexibility that enables property optimization makes it difficult to identify single-phase stability windows and oxygen vacancy energetics across dopant space using density functional theory (DFT) alone. Here, we integrate electrospun HEO nanofiber experiments with universal machine learned interatomic potential (uMLIP/UMA) modeling and stability descriptors to connect synthesis outcomes with composition–stability predictions.

Experimentally, Mn- and Ti-doped equiatomic (CoCuMgNiZnX)O nanofibers (X = Mn, Ti) preserve a continuous, interconnected network after calcination, exhibiting mild crystallization-induced surface roughness and high BET surface areas. XRD verifies a single phase fcc rocksalt structure for Mn-doped fibers, whereas achieving a fully single-phase rocksalt state in Ti-doped fibers using Ti addition alone remains challenging, consistent with a narrower stability margin.

Computationally, we employ uMLIP/UMA (CHGNet and eSEN) to map single-phase stability regions using descriptors based on mixing enthalpy and first-nearest-neighbor bond-length disorder [1].

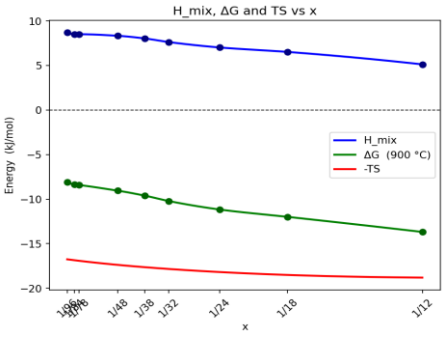


Figure 1. Impact of concentration of titanium (x) in HEO to Gibbs free energy

In the MgCoNiCuZn-Mn compositional space, the model predicts a stable single-phase region at low Mn contents that transitions to multiphase behavior as Mn increases. In contrast, coupled Ti-Li substitution enhances thermodynamic stability, with configurational entropy contributions becoming increasingly important in lowering Gibbs free energy at elevated temperatures (≈900 °C). uMLIP defect calculations further reveal strong cation control of oxygen vacancy formation energies. [2] Overall, this combined experimental-computational framework positions uMLIP as a practical route to predict phase boundaries and vacancy stability and to interpret experimentally observed single- versus mixed-phase outcomes in doped rocksalt HEO nanofibers.

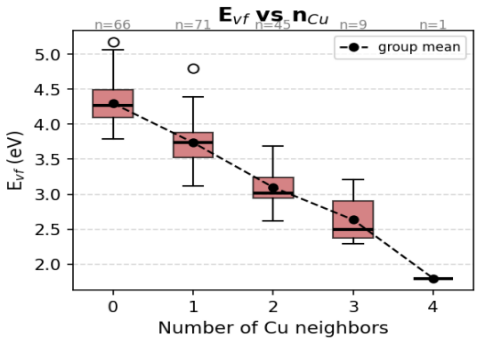


Figure 2. Vacancy formation energy dependence on copper content

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