Designed Metal Release From Complex Metal Oxides

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Complex metal oxides have widely transformed the current state of technology across the globe. The most widespread examples are the electroactive components of Li-ion batteries found in portable electronic devices. As the number of portable devices is projected to increase, so too will the inadvertent release of complex metal oxide nanomaterials into the environment. To this end, there is a fundamental knowledge gap in developing sustainable nanotechnology. This is due to the fact that there is not yet a systematic method to predict how the properties of a complex metal oxides will vary with changes in chemical environment. Based on Hess's Law, we have established such a method, combining DFT-computed total energies and experimentally adjustable reaction conditions[1]. This approach predicts the thermodynamics of metal release from complex metal oxides. Our DFT-based energetics and electronic structure calculations have shown that the oxidation states of the metals in these materials adjust according to the chemical environment. The oxidation states also determine the stability of that metal in the lattice of the material, and can facilitate dissolution of the potentially toxic ions into aqueous environments. We focus on the materials found in a Li-ion battery cathode, namely $LiCoO_2$ (LCO) and its compositionally tuned variants with general chemical formula $Li(Ni_xMn_yCo_z)O_2$ (NMC)[2]. Using dissolution energetics, projected density of states, and band structure calculations, we propose that adjusting surface terminations, compositions and pH will change the oxidation states of the metals. Our further investigations show that increasing the amount of Mn in the NMC lattice will facilitate dissolution from all the metals[3], whereas increasing the amount of Ni will stabilize the lattice and have similar dissolution trends as the equistoichiometric NMC[4]. Since the release of Ni, Mn, and Co has shown to have adverse biological effects[5], we employ database mining along with our developed methodology, to put forth a new set of materials where we have replaced Ni, Co, and Mn with metals that will keep the same functionality while reducing biological impact.

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