Density-functional Study of the Kinetics of Chemical Transformation of Cobalt to Cobalt Oxides

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Transition metal oxides are particularly interesting materials because they exhibit unique magnetic, optical and chemical properties. Cobalt oxides, in particular, have recently received increased attention due to their catalytic properties and potential as a promising anode material in Li-ion batteries.[1] Even though we know a lot about the structure, synthesis techniques, and properties of these oxides, very little is known about the mechanisms and kinetics of the reactions that occur as cobalt is oxidized.

Here, we present a study of the chemical transformation of ε-Co metal into CoO and Co_3O_4, using density functional theory.[2] The goal of our study is to determine (i) the kinetics of the nanoscale transformation, (ii) the diffusion processes during chemical conversion, and (iii) the structural and morphological changes that occur during the reaction.

We combine our computational results with experimental characterization data to elucidate the dominant diffusion mechanism in these reactions. We come across an interesting indirect-exchange mechanism for the diffusion of O in ε-Co that has a lower energy than simple vacancy and interstitial diffusion mechanisms. The results of the activation energies of diffusion of Co and O in the oxides explain the occurrence of the nanoscale Kirkendall effect which leads to hollowing of the nanoparticles.

[1] D.-H. Ha, M. A. Islam, and R. D. Robinson, Binder-Free and Carbon-Free Nanoparticle Batteries: A Method for Nanoparticle Electrodes without Polymeric Binders or Carbon Black. *Nano Lett* **12**, 5122–5130 (2012).

[2] D.-H. Ha, L. M. Moreau, S. Honrao, R. G. Hennig, and R. D. Robinson, The Oxidation of Cobalt Nanoparticles into Kirkendall-Hollowed CoO and Co_3O_4: The Diffusion Mechanisms and Atomic Structural Transformations. *J. Phys. Chem. C*, in print (2013).