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Engineering disorder into heterogenite-like cobalt oxides by phosphate doping: Implications for the design of water oxidation catalysts

Metal oxides are amongst the best known and most extensively studied water oxidation catalysts. Many metal oxide materials function best in a proton accepting electrolyte such as a borate or phosphate buffer. The inclusion of these electrolyte anions in the bulk material (in small amounts) is recognized to result in amorphous metal oxides with “molecular-like” structure. The importance of these disordered “molecular-like” metal oxides in water oxidation catalysis has been difficult to deconvolute from the effects of the electrolyte used for deposition. In this study we have synthesized as series of heterogenite-like cobalt oxides with different levels of phosphate doping (0 - 9%) and carefully characterized the materials using a range of analytical techniques including, XAS, TEM and XRD. It was found that phosphate doping systematically altered the nano-scale and molecular-level structure of the materials, with the materials changing from nano-crystalline to amorphous as the level of phosphate doping increased. The changes were correlated with reactivity for water oxidation catalysis and as sacrificial oxidants. It was found that the most disordered materials were most reactive in sacrificial reactions, however, less effective for water oxidation catalysis. The result demonstrate how subtle structural ordering effects can significantly impact on reactivity.

Keywords or phrases (comma separated)

Cobalt oxide, water oxidation, water splitting, renewable energy

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