

Surface energy modulation of PdCu nanocatalysts via the crystal structure change for lithium-oxygen batteries

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Palladium-copper (PdCu) alloys have two representative crystal structures; one is body-centered cubic (bcc) and the other is face-centered cubic (fcc), even though both Pd and Cu originally have the fcc crystal structure. The fcc PdCu alloys form a solid solution wherein the Pd and Cu atoms are randomly distributed over the fcc lattice sites, whereas the bcc PdCu alloys have alternating Pd or Cu atoms between the body centered and corner sites of the bcc structure.

In particular, the bcc PdCu alloys have been expected to show generally superior performance to the fcc PdCu alloys as the electrocatalyst for lithium-oxygen batteries. The higher activity of bcc PdCu alloys has been attributed to its unique ordered structure, whereby the isolated Pd atoms – the active site for the catalytic reaction – are on the surface and are richer in electron density due to its higher electronegativity than Cu on the Pauling scale. However, the electrochemical performance between fcc and bcc PdCu nanoparticles (NPs) have never been rigorously compared due to the difficulties in achieving size control, since crystallites larger than 20 nm favor the ordered bcc structure with lower symmetry. Most of the bcc PdCu alloys reported have been synthesized from alloys in the fcc phase by structural transformation using an annealing or seed-growth method, leading to the inevitable growth of crystallite size, uneven surface structure and broad particle size distribution. The theme of this work is to develop the synthetic strategy to exercise size control over the fcc and bcc structures, thus enabling a proper comparison of their respective electrochemical performance.

In this study, we successfully synthesized fcc and bcc PdCu alloys in the nanoscale through precisely adjusting the driving force for reducing the organometallic precursor. The bcc PdCu NPs with higher surface energy govern the thermodynamics of the growth of the discharge products and greatly improved their battery performance based on density functional theory calculation and experimental results. This study provides the critical descriptor on material design in the perspective of modulating surface structure via crystal structure to tune its intrinsic properties.