Dealloying Pt bimetallic catalysts at constant electrode potentials and its effect on the oxygen reduction reactivity

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Optimization and atomistic understanding of the dealloying process of non-noble metal rich Pt bimetallic nanoparticles is key to further improve their activity and stability for the oxygen reduction reaction (ORR)[1-8]. Here, we synthesized two well alloyed and near-monodisperse $PtNi_3$ alloy nanoparticle catalysts with mean particle sizes of ~6 nm and ~20 nm, which exhibited high initial mass activity towards oxygen reduction reaction. These catalysts were dealloyed at various constant electrode potentials for 24 hours and their structural changes were studied by electrochemical votlammetric measurements, transmission electron microscopy (TEM) and energy dispersed X-ray spectroscopy (EDX). We uncovered surprising trends in the particle surface compositions, bulk compositions and morphology, in particular nanoporosity, of the dealloyed $PtNi_3$ catalysts as a function of the applied constant potential. A simple atomistic model is proposed to explain our results and, based on this; an optimized constant dealloying strategy was explored to achieve both enhanced catalytic activity and increased durability of the $PtNi_3$ catalysts.

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