Structural Changes in $Pt_5MnFeCoNiCu$ Solid Solutions and Intermetallics during Electrochemical Oxygen Reduction

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Platinum is the best-performing catalyst material for the oxygen reduction reaction (ORR). However, it is scarce and expensive. Therefore, reducing platinum loading while maintaining catalytic activity and stability remains a central challenge in oxygen reduction reaction (ORR) electrocatalysis, as catalysts containing less than ~75 at.% Pt often show reduced performance [1]. High-entropy alloys offer a promising strategy to lower Pt content by incorporating multiple transition metals while preserving catalytic performance [2]. Here, we investigate the structural evolution of low-platinum (50 at.% Pt) $Pt_5MnFeCoNiCu$ nanoparticles synthesized as either high-entropy solid solutions (HESOSO) or high-entropy intermetallics (HEI) under electrochemical ORR conditions.

Operando X-ray total scattering experiments were performed at Diamond Light Source using a custom-built gas diffusion electrode setup that mimics membrane electrode assembly environments used in commercial fuel cell applications [3]. Sequential Rietveld refinement of diffraction data was used to track bulk structural changes, while pair distribution function (PDF) analysis probed local atomic order.

The as-synthesized HESOSO catalysts are well described by a face-centred cubic (*fcc*) structure, whereas the HEI samples require a two-phase model consisting of an intermetallic body-centred tetragonal (*bct*) phase and a *fcc* phase. During electrochemical testing, both catalyst systems retain their initial crystallographic structures. PDF analysis confirms that the local coordination environments remain largely unchanged. The most pronounced structural changes occur upon electrolyte introduction, where lattice parameters contract. During continued operation, the lattice parameters gradually increase, consistent with preferential dissolution of 3d elements, as confirmed by *online* ICP-MS measurements. Simultaneously, the coherent domain size increases while refined scale factors decrease, indicating preferential degradation of smaller crystallites and net catalyst loss through particle dissolution and detachment. While both catalysts degrade via similar mechanisms, the HESOSO particles are more strongly affected than the HEI despite the latter exhibiting higher catalytic activity. The preservation of bulk and local structure suggests that the observed loss of ORR activity primarily arises from degradation of the catalyst layer, likely caused by carbon oxidation or mass-transport limitation effects such as flooding. These results highlight high-entropy alloys – particularly the intermetallics - as promising low-Pt ORR catalysts as well as the value of combining *operando* reciprocal and real space data analysis to investigate the origin of catalyst degradation.

[1] Alfaifi et al. *ACS Catal.* **2025**, 15, 9301−9345
[2] Sun et al, *ACS Mater. Au* **2024**, 4, 547−556
[3] Wiberg et al, *Chimia* **2024**, *78*, 344