Crystal structure of Pt-Cu nanoparticulate oxygen reduction reaction electrocatalysts

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Proton exchange membrane fuel cells are a viable alternative to fossil fuel-powered engines in the energy and mobility sector. However, the cost of the electrocatalyst for the oxygen reduction reaction (ORR) still poses an issue, as it commonly contains scarce noble metals, like platinum. Supported Pt-alloy nanoparticles are now commonly used to lower the amount of Pt but retain good ORR performance[1]. Despite numerous studies on structure-property relationships of nanoparticulate electrocatalysts, the effects of selected structural features on the catalytic activity and stability remain unexplored. Ensembles of such nanoparticles typically vary in size, shape, composition, crystal structure, and defects, all of which can impact their performance. Therefore, advanced characterization methods are needed to obtain both bulk and local information about the catalyst structure to properly correlate it to its properties. In this presentation, I will focus on studying the crystal structure of carbon-supported platinum-copper nanoparticulate electrocatalysts, used for the ORR, specifically on anti-phase boundaries inside the catalytic nanoparticles[2]. Those planar defects, contributing to chemical disorder, were previously described for a bulk alloy, but not for a nanoscale catalyst. X-ray powder diffraction patterns were used in conjunction with simulations and Rietveld analyses to reliably determine the defect placement. Electron diffraction and atomically resolved scanning transmission electron microscopy (STEM) were used to confirm the defect presence locally, and ORR performance was evaluated for several platinum-copper analogs with and without anti-phase boundaries. Furthermore, I will discuss what STEM and its advanced modalities, such as 4D-STEM, can offer in the context of nanoparticulate electrocatalysts using a platinum-copper system as an example, especially to show how identical location microscopy brings added value to stability studies. This work represents a step towards a deeper understanding of electrocatalysts' structure-property relationships by providing insight into the crystal structure of alloyed nanoparticles.

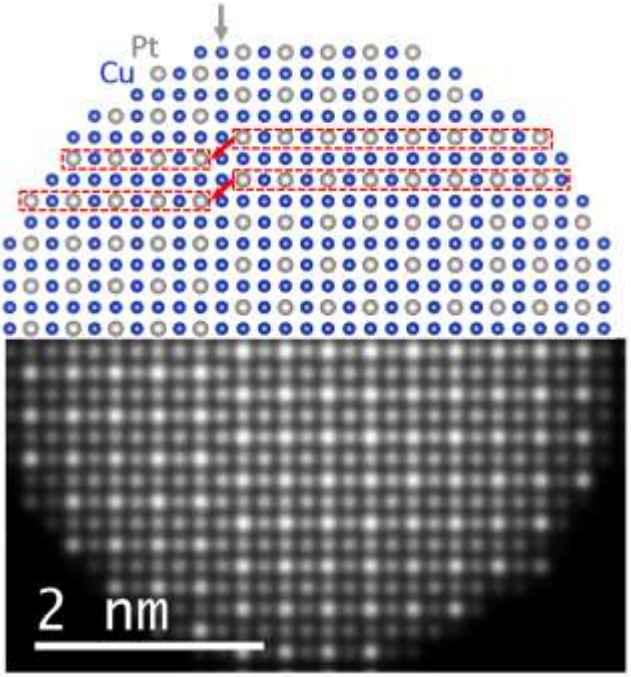

Figure 1. A Pt-Cu nanoparticle with an anti-phase boundary, depicted with a simulated STEM image, and the model, used for the simulation

References

1. M. Janssen, P. Weber, M. Oezaslan, *Curr. Opin. Electrochem.* **40** (2023) 101337 https://doi.org/10.1016/j.coelec.2023.101337.
2. A. R. Kamšek, A. Meden, I. Arčon, P. Jovanovič, M. Šala, F. Ruiz-Zepeda, G. Dražić, M. Gaberšček, M. Bele, N. Hodnik. *Mater. Today Nano.* **23** (2023) 100377 https://doi.org/10.1016/j.mtnano.2023.100377.