Understanding strain and composition effects in fuel cell catalysts using advanced electron microscopy and DFT

Alessandro Zanre[1], Dr. Aaakash Varambhia[2], Dr. Dogan Ozkaya[2], Dr. Xiaonan Luo[3], Prof. Sergio Lozano-Perez[1], Prof. Rebecca J. Nicholls[1], Prof. Peter D. Nellist[1]
[1]Department of Materials, University of Oxford, , United Kingdom, [2]Johnson Matthey Technology Centre, , United Kingdom, [3]Contemporary Amperex Technology Co., Limited, , P. R. China

Background and aims
Hydrogen fuel cells are an important technology for decarbonising road transport and shipping. Their efficiency is limited by the oxygen reduction reaction (ORR), which requires catalysts to achieve acceptable performance for the cell. The state of the art ORR catalysts are Pt-X nanoparticles, where X is another transition metal. These nanoparticles have a core-shell structure, consisting of an alloyed Pt-X core surrounded by a Pt rich shell. They perform much better as ORR catalysts than pure Pt nanoparticles, however the origins of this activity enhancement are not fully understood. The main factors that are hypothesised to be responsible are ligand effects, where chemical differences between Pt and X modify the electronic properties of the catalyst surface, and strain effects, where changes in nanoparticle size and shape induced by the size mismatch between Pt and X lead to changes in electronic structure. Core-shell nanoparticles have been observed to have a high degree of strain at the surface which affects the d band structure at the nanoparticle surface, which is crucial in determining O binding strength and ORR catalytic activity. Complex strain states with a significant shear component have been observed in the outer layers of core-shell nanoparticles via atomic resolution scanning transmission electron microscopy (STEM); while the effect of volume changing normal strains on catalytic activity has been widely studied, those of shape changing shear strains have been largely overlooked in the literature. Our key aim in this work is to use computational modelling to understand the electronic properties of experimentally observed nanoparticle structures, and the effect of these properties on catalytic activity, as a step towards better understanding the structure-property relationship and improving fuel cell catalyst design.

Methods
Microscopy: Alloyed Pt-Co core-shell fuel cell catalyst nanoparticles on C have been provided by Johnson Matthey. Atomic resolution high angle annular dark field STEM (HAADF-STEM) with EDX and EELS has been performed on these nanoparticles to understand their structure and composition at the atomic level. Column positions relative to a reference grid which is fitted to a nanoparticle structure have been used to measure variations in strain across its extent. The compositional information allows the elastic strain to be distinguished from lattice parameter changes arising from different local alloy compositions.

Computation: DFT calculations have been performed using CASTEP 22.11 on pure Pt to measure the effect of normal and shear strains on the d band centre. All calculations were performed with the PBE functional. Equilibrium bulk and slab structures were first obtained by geometry optimisation. Strain states representative of those seen in STEM images of catalyst nanoparticles were then applied and the d projected PDOS and d band centre of these strained structures were calculated and compared.

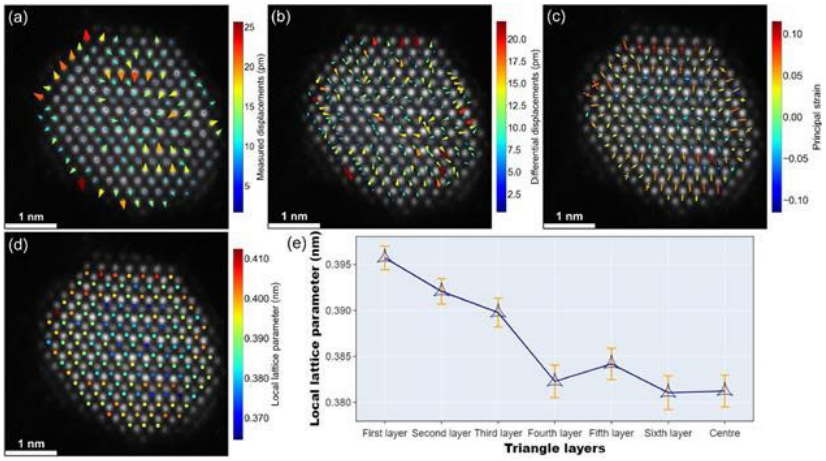
Results
Atomic resolution HAADF-STEM measurements of catalyst nanoparticles have shown that the outer layers exhibit both normal and shear strains relative to the reference structure that was

fitted to the nanoparticle. DFT calculations have shown that the shear strains typically observed in catalyst nanoparticles are unlikely to have a significant effect on their electronic properties.

Conclusions

The ability to reliably map strain at the atomic scale for nanoparticles is an important step in linking structure to activity, and ultimately determining the optimal surface structure for ORR catalysts. The independence of electronic properties on small shear strains suggests that unit cell volume is a key descriptor of catalytic activity.

Graphic:



Keywords:

HAADF-STEM, DFT, catalysis, strain

Reference:

Luo, X. et al. (2022), Ultramicroscopy, 239, 113561