Advanced Methodology for Charge Density Mapping of Supported Nanoparticle Electrocatalysts Using 4D STEM

Lazar Bijelić, Ana Rebeka Kamšek, Francisco Ruiz Zepeda, Goran Dražić, Nejc Hodnik

National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia,
E-mail: lazar.bijelic@ki.si

The environmental impact and finite nature of fossil fuels make them unsuitable for future energy frameworks. Hydrogen fuel cells are crucial for energy storage and transportation within these frameworks. Proton exchange membrane fuel cells convert hydrogen and oxygen into water, generating electrical energy. Platinum nanoparticles supported on carbon are highly effective for the hydrogen oxidation reaction, but finding suitable materials for the oxygen reduction reaction (ORR) remains challenging due to issues with activity and durability. Enhancing electrocatalyst activity can be achieved by increasing surface area or altering material composition, though long-term stability is often compromised by catalyst degradation. One strategy to address this is using catalyst supports that offer more than substrate functionality. Metal-support interactions, which affect the nanocatalysts properties through strain or electronic structure changes, can improve electrocatalytic performance. Currently, few methods can directly characterize these interactions. 4D scanning transmission electron microscopy (4D STEM) allows for localized analysis of nanoparticle-support interactions by using a fast, pixelated electron detector to capture diffraction patterns at each probe position in an STEM image. The divergence of the center of mass (dCOM) of the electron probe is proportional to charge density, allowing visualization of charge redistribution at the catalyst-support interface. However, factors like particle orientation and support thickness affect dCOM image contrast, complicating its direct interpretation as charge density. This research develops a methodology to determine the charge density distribution of supported nanoparticle electrocatalysts, using platinum on graphene as a model system for its simplicity and uniform thickness. This methodology is then applied to more complex systems, such as nanocatalysts supported on titanium oxynitride and amorphous carbon.