Atomic-level perspective on the functionality of nanoalloy catalysts inside operating fuel cells by combined in operando high energy x-ray spectroscopy and total scattering

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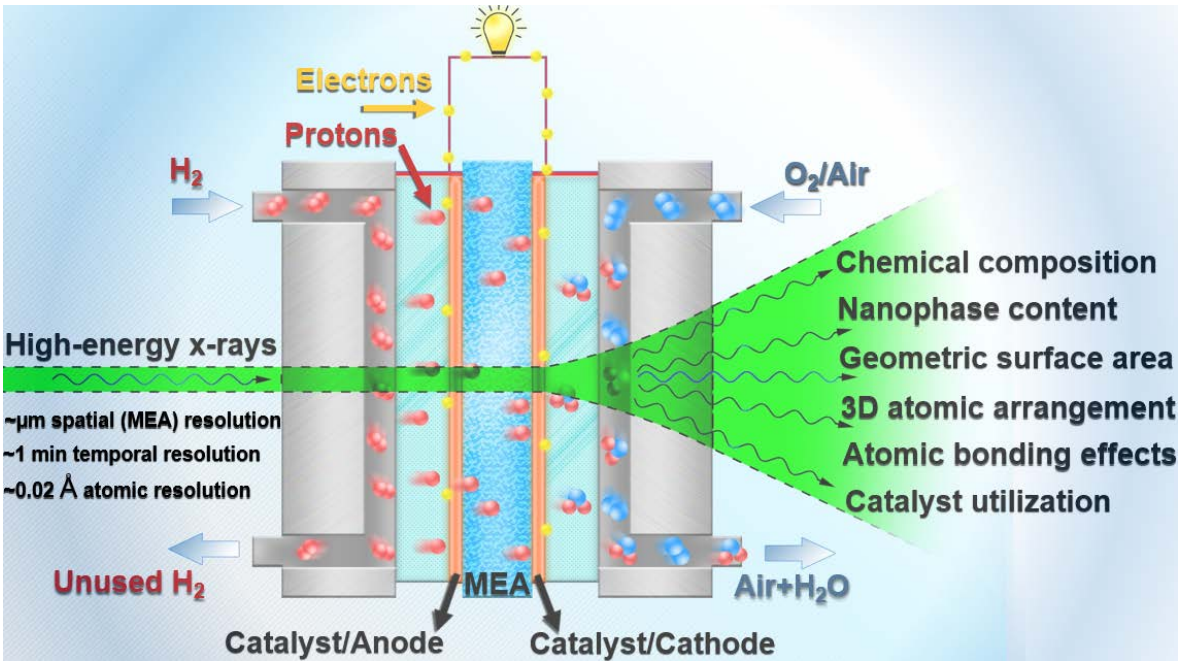
Abstract: The activity and stability of nanoalloy catalysts for the chemical reactions driving devices for clean energy conversion, such as the oxygen reduction reaction (ORR), depend critically on optimizing the composition, surface area and phase type of the nanoalloys, including the bonding interactions between the constituent atoms, for the harsh operating conditions inside the devices. We present results from *in operando* high-energy x-ray diffraction (HE-XRD) study coupled by atomic pair distribution function (PDF) analysis and energy dispersive x-ray spectroscopy (EDS) on the concurrent atomic-scale changes and decay of the ORR activity of Pd-Sn, Pt-Ni-Cu nanoalloy catalysts as they function at the cathode of a proton exchange membrane fuel cell (PEMFC).

Here we address the problem by studying the atomic-level evolution of noble metal-based nanoalloy catalysts for ORR as they function at the cathode of an actual proton exchange membrane fuel cell (PEMFC). In particular, we use 1-min time and µm-sized space resolved energy dispersive x-ray spectroscopy (EDS) and total x-ray scattering to obtain precise information about the chemical composition, geometric surface area, phase content, 3D arrangement and strength of interaction between the constituent atoms of the nanoalloys. Besides, we evaluate the utilization of the nanoalloy catalysts by measuring variations in their chemical composition and mass distribution over the PEMFC cathode. Concurrently, we measure the current output of the cell that reflects the ORR activity of the nanoalloys. Experimental x-ray data show that the atomic-level changes of nanoalloys can occur simultaneously over different time frames, ranging from minutes-long structural phase transitions to hours-long alterations in chemical composition, and in multiple dimensions, ranging from repetitive sub-Å atomic displacements to nm-sized particle growth. Besides, x-ray data reveal considerable exchange of atomic species between individual nanoalloy particles, that is, effective mass transport across the PEMFC cathode. Experimental catalytic data show that the ORR activity of nanoalloys closely tracks the atomic-level changes they undergo during the PEMFC operation. Ultimately, we demonstrate the great potential of combined in operando EDS and PDF studies as a tool for guiding the effort to produce more efficient and affordable nanocatalysts for energy related applications.



Mechanistic description of ORR at the cathode of a PEMFC and HE-XRD experiment on the PEMFC cathode catalyst. Hydrogen (H_2) molecules are delivered to the PEMFC anode and split into protons and electrons via a reaction known as the hydrogen oxidation reaction (HOR). The resulting protons permeate through a membrane electrode assembly (MEA) to the PEMFC cathode while electrons reach it via an external circuit, thus generating current output. Oxygen (O_2) molecules reduced at the PEMFC cathode react with the protons arriving at it, forming water. The reaction, known as ORR, is six orders of magnitude slower than HOR, necessitating a very efficient catalyst, e.g. noble metal-transition metal alloy particles, for speeding it up. Thanks to their high-flux and energy, synchrotron x-rays are able to probe the PEMFC cathode catalyst with sub-Å precision, in both time (~ 1min) and space (μm-sized) space resolved manner. Experimental data provide information for the chemical composition, nanophase content, geometric surface area, 3D arrangement and bonding interactions of atoms constituting the cathode catalyst as it functions under actual operating conditions. The catalyst utilization, related to the chemistry and mass distribution of nanoalloy particles over the MEA, is also assessed.

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Bio

Research Assistant working in material science field. Joined Prof. Valeri Petkov group on 2015. Skilled in HE-XRD, EDX, XPS, data analysis and data mining. The latest project I'm working on is about the structural dynamics and activity of nanocatalysts inside fuel cells by high energy X-ray diffraction (HE-XRD) coupled with in-operando atomic pair distribution studies (PDF), cyclic voltammetry (CV), X-ray energy depressive spectroscopy(EDX) and molecular dynamics (MD). To reveal the activity and stability of nanoalloy catalysts for chemical reactions driving devices for clean energy conversion.

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