

APPLICATION NOTE: POSEIDON SELECT

Direct Observation of Corrosion in Nanocube Electrocatalysts



INTRODUCTION

The implementation of non-petroleum based energy sources is becoming increasingly important everyday as global energy consumption increases by ~125 million metric tons of oil equivalent every year¹ and carbon emissions globally increase by ~200 million metric tons from fossil fuels every year (Figure 1).² Thus, research in cleaner, efficient energy technologies is critical in the developing world. One such promising technology is fuel cells, which have at least 90% less pollutant emissions than petroleum-based energy sources and can reach conversion efficiencies as high as 60%.³ However, commercially preserving that high conversion efficiency remains challenging. While much progress has been made in fuel cell technology, there are still some areas of research necessary to make it a viable, widespread energy source. These areas include: i) using lower cost materials, ii) limiting the degradation of the fuel cell materials, and iii) increasing the activity and efficiency of the fuel cells.

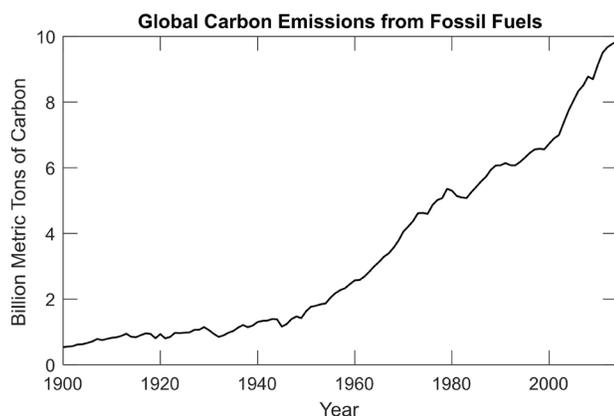


Figure 1: Global carbon emissions from fossil fuels 1900-2014.²

In short, fuel cells convert chemical energy into extractable electricity. For this to occur, fuel cells have three main components: an anode, a cathode, and an electrolyte. Reactions occur at the cathodes and anodes that result in the production of electrons and protons; a process that is sped up by the use of

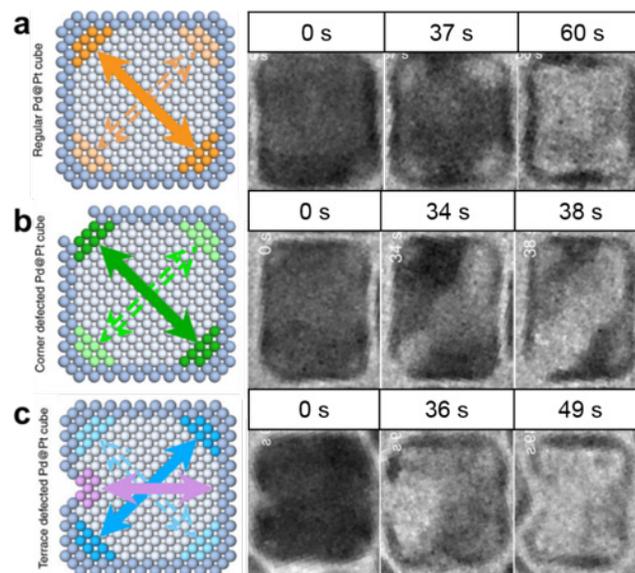


Figure 2: Corrosion process of regular (a), corner defected (b), and terrace defected (c) nanocubes. Left panel displays illustration of atomic structures. Right panel displays TEM micrographs showing the corrosion process of Pd atoms in single Pd-Pt nanocubes with indicated time points. Each nanocube is about ~10 nm in length.

catalysts. The main catalyst used in fuel cells at the cathode is platinum (Pt) nanoparticles. Increasing and maintaining the surface area of these nanoparticles is crucial to improving the fuel cell performance. A promising way to achieve increased platinum catalytic performance, decreased material cost, and longer material lifetime is by implementing nanocage morphologies. However, controlling the formation and stability of these morphologies at such small scales can prove to be very difficult when the researchers do not have a fundamental understanding of the particle synthesis mechanisms. Thus, study of the kinetics of nanocage synthesis is critical to the eventual control and optimization of the process.

EXPERIMENT

The researchers synthesized core-shell Pd-Pt nanocubes and then targeted the corrosion of the inner Pd metal to form Pt nanocages. Due to advances in *in situ* transmission electron microscopy (TEM), they

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were able to precisely study in high-resolution, the corrosion kinetics of the Pd core in typical wet, synthesis conditions. From these experiments, they gleaned crucial information on the activity of the different crystallographic locations, as well as make valuable suggestions on the future design of materials structures for optimized electrocatalysis.

RESULTS

The researchers observed two different corrosion processes occurring throughout the nanocage synthesis: galvanic dissolution and halogen etching. Galvanic dissolution is the migration of atoms through the nanoparticle material and halogen etching is the removal of material by reaction with halogen species. For halogen etching to occur, there needs to be an introduced defect in the nanocube shell to expose the Pd core. The combination of the two corrosion processes resulted in different final nanocage morphologies (Figure 2). The kinetics of corrosion were intensely quantified, and the authors found that the corrosion rate process has three stages determined by the corrosion method (Figure 3). Namely, halogen etching resulted in a faster corrosion compared to galvanic dissolution.

Importantly, the researchers found that when only galvanic dissolution occurred, the Pd core continued to etch until the nanocages were no longer stable and collapsed into hollow spheres; a transformation that should ideally be avoided to maintain the high number of active Pt sites offered in nanocages. However, the introduction of halogen etching inhibited the ability of the material to undergo galvanic dissolution, and thus avoided over-corrosion and nanocage collapse. The researchers now know that the introduction of nanocube defects can avoid this nanocage collapse, increasing both the lifetime of the fuel cell material as well as the activity of the material.

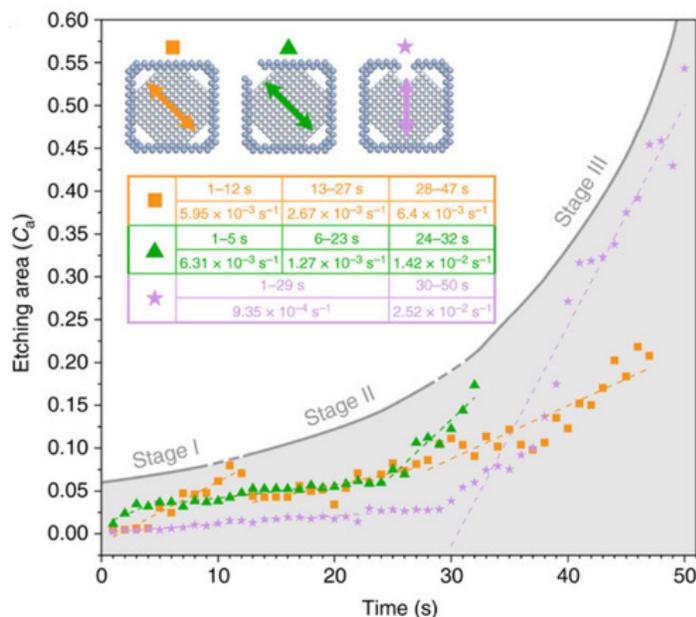


Figure 3: Corrosion process of regular (a), corner defected (b), and terrace defected (c) nanocubes. Left panel displays illustration of atomic structures. Right panel displays TEM micrographs showing the corrosion process of Pd atoms in single Pd-Pt nanocubes with indicated time points. Each nanocube is about ~10 nm in length. [Supplementary video](#)

CONCLUSIONS

Using *in situ* TEM, the researchers viewed the real-time corrosion process of nanocubes into nanocages. Through high-resolution observation, the kinetics of the corrosion in its real-application conditions were quantified. This leads to conversion efficiency and lifetime improvements in the electrocatalysts and directs the use of less high-cost materials for the generation of fuel cells. The research reported here simultaneously makes fuel cells more commercially viable, while still increasing the catalytic activity of the materials within them for improved energy conversion.

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KEY TAKEAWAYS

- Novel *in situ* observation of materials synthesis aids in decreasing cost of fuel cell generation, making fuel more commercially viable.
- Improving fuel cell technology can aid in the decrease of the emission of fossil fuels by being a different “green” energy source.
- A new understanding of the dynamic processes in nanocage corrosion in liquid synthesis conditions enables optimized material generation for electrocatalysis.

Reference: [Shan, Hao, et al. “Nanoscale kinetics of asymmetrical corrosion in core-shell nanoparticles.” *Nature Communications* \(2018\).](#)

¹International Energy Agency. “Key world energy statistics.” IEA Publications (2017).

²Boden, Thomas, et al. “Global, Regional, and National Fossil-Fuel CO₂ Emissions.” Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. (2017).

³Wang, Yun, et al. “A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research.” *Applied Energy* (2011).