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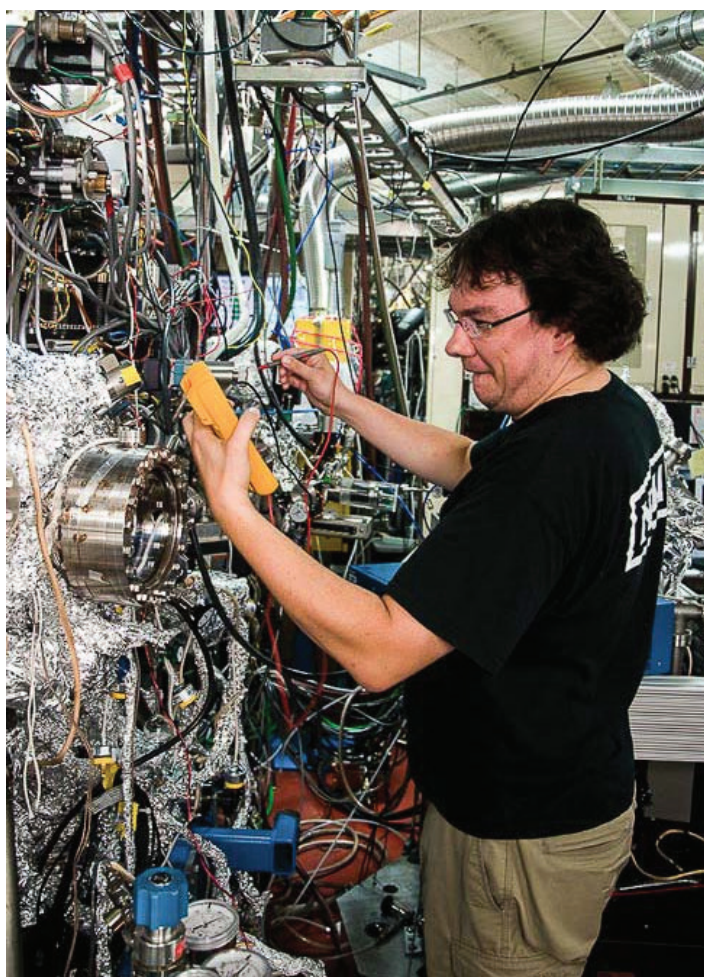
SCIENCE HIGHLIGHT

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ALS X-Rays Shine a New Light on Catalysis

Electrocatalysts are responsible for expediting reactions in many promising renewable energy technologies. However, the extreme sensitivity of their surface redox states to temperatures, to gas pressures, and to electrochemical reaction conditions renders them difficult to investigate by conventional surface-science techniques. Recently a team of Stanford and Berkeley Lab researchers used x-rays at the ALS in a novel way to observe the behavior of electrons during technologically-important chemical reactions in metal oxide electrocatalysts. What they learned has upended long-held scientific understanding of how these catalysts work.

Many of today's most promising renewable energy technologies—fuel cells, water splitters, and artificial photosynthesis—rely upon catalysts to expedite the chemical reactions. Catalysts are materials that enhance chemical reactions without being consumed in the process. Ceramic-like metal oxides, such as iron oxide (a material similar to rust) are desirable as catalysts because they are more abundant and more stable than typical catalysts made of rare metals like platinum, ruthenium and rhodium. Although they may be more abundant, however, metal oxides are also less sci-



Lead author Dr. David Mueller at the ALS using x-rays to characterize working fuel cells.

tifically understood than their metallic counterparts.

Electrochemical reactions involving oxygen gas molecules, in particular, are ubiquitous in energy conversion and storage technologies. A techno-

logically- important class of oxygen electrochemical reactions is one that simultaneously reduces oxygen molecules to and incorporates them as solid-state oxygen ions and vice versa. At the ALS, researchers

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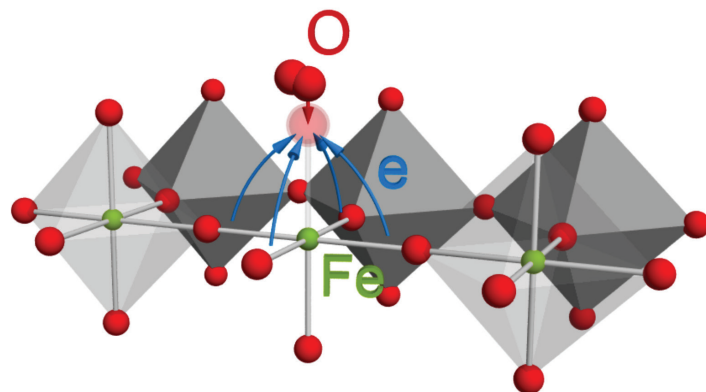
were able to directly observe redox processes in thin-film iron and cobalt perovskite oxide electrocatalysts using surface-sensitive, x-ray absorption spectroscopy while the electrochemical reactions took place.

Redox Redux

Catalysts play a fundamental role in our lives, though few outside the community of researchers and engineers who study them know much about how they work. Metal oxides, in particular, are leading candidates for use as catalysts at the heart of a fundamental chemical reaction known as reduction-oxidation, or “redox” for short. Redox reactions are key to renewable energy uses.

One of the best examples is water splitting. Electricity generated from the sun via solar panels is passed through water. The electric current separates (“splits”) the water into its two constituent elements: environmentally beneficial oxygen and clean-burning hydrogen. The hydrogen can then be stored and later burned as fuel to generate electricity when the sun is not shining.

A major hurdle on the path to these renewable energy applications has been the catalyst. The Stanford/LBNL team’s research at the ALS used x-rays to look closely at these reactions.



X-rays following electrons during oxygen incorporation and release reactions in perovskites show that oxygen ions are the redox partner, not the transition metal ions.

narrow oxygen-ion electronic state exchanges electrons with the molecular oxygen. This result highlights the importance of surface anion-redox chemistry in transition-metal oxides electrocatalysts.

The findings could guide the search for new and better catalysts. Researchers are now looking to develop new catalysts by modifying the oxygen ions in these systems. Previously, it was challenging to study how gas molecules,

particularly oxygen, interacted with the catalyst because researchers couldn’t include them in the experiments. Unique instruments at the ALS allowed the researchers to follow the electrons as they do their work and to better understand how they behave during the reactions. What they have learned is critical to fundamental-level understanding of catalysts and could lead to exciting new directions in catalyst design.

In contrast to the conventional view that the transition metal cations are the dominant redox-active centers, researchers found that the oxygen anions near the surface are a significant redox partner to molecular oxygen due to the strong hybridization between oxygen 2p and transition metal 3d electronic states. The research proposes that a

