

A Surface Treatment for Improving Fuel-Cell Cathodes

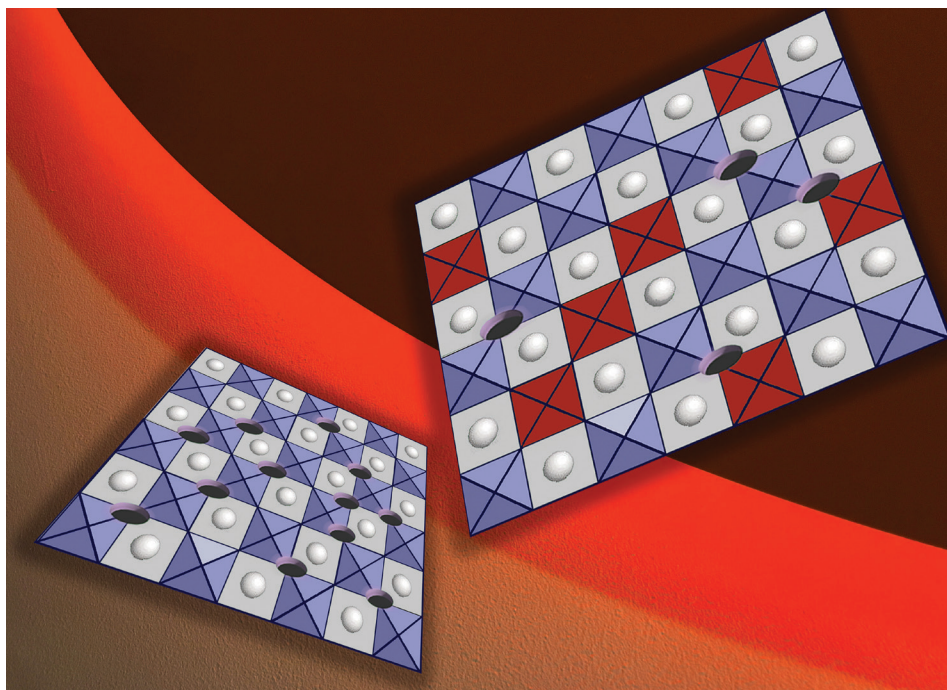
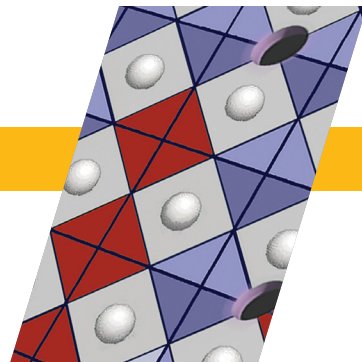


Diagram depicting the way a new surface treatment can improve the efficiency and longevity of materials for use in applications such as fuel-cell electrodes. At left is an unmodified cathode surface with a large concentration of oxygen vacancies (holes). At right is a cathode surface with modified cations (red squares), reducing the concentration of oxygen vacancies and significantly slowing down the rate of reactions that could degrade the surface and impair its performance. (Courtesy of Felice Frankel, MIT.)

Solid-oxide fuel cells (SOFCs) are a promising path toward the “clean” conversion of chemical energy to electrical energy with little or no carbon dioxide emission. With the help of the ALS, researchers from MIT recently found a way to treat SOFC cathode surfaces so that they perform better and last longer. Ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) and ambient-pressure x-ray absorption spectroscopy (AP-XAS) were critical to the researchers’ success in uncovering the physical principles behind this improvement, which can reduce energy losses in fuel cells by half, making them twice as efficient and less costly.

SOFCs are devices that convert the chemical energy in fuels (hydrogen, syngas, natural gas, etc.) directly into electricity, with very high efficiency and zero exhausted pollutants. However, one limiting factor preventing the wide deployment of this clean energy-conversion technology is the degradation of the cathode, usually made of a perovskite oxide, under operating conditions of high temperature (greater than 500 °C) in an oxidizing atmosphere (air). Earlier work had found that an important reason for this degradation is the segregation and phase separation of dopants (i.e., strontium), deposited on the cathode surface to catalyze fuel-cell reactions. The segregated strontium further

A Solid Alternative

Like batteries, fuel cells generate electrical energy from chemical energy. Unlike batteries, fuel cells don’t run down when exhausted, but are designed to work as long as they are supplied with fuel, which could be anything from solar-produced hydrogen to gassified coal. There is no combustion involved, only chemical reactions with water and heat as the sole byproducts. Solid-oxide fuel cells (SOFCs) in particular operate at high temperatures, and the heat generated can be “recycled” to increase efficiency to over 80%. Thus, SOFCs are good options for applications such as electricity generation by auxiliary power units, distributed generation systems, and utility-scale central power stations.

This work by Tsvetkov et al. presents a new, practical, and scalable approach that potentially solves a great barrier to the widespread implementation of SOFCs: the durability of SOFC cathodes. By understanding how the active cathode materials degrade, the researchers were able to intelligently modify their surfaces to improve performance and extend cathode life. When this approach is introduced into real SOFC devices, the researchers believe that the durability of SOFCs can be increased significantly, helping to advance the development of a clean-energy infrastructure.

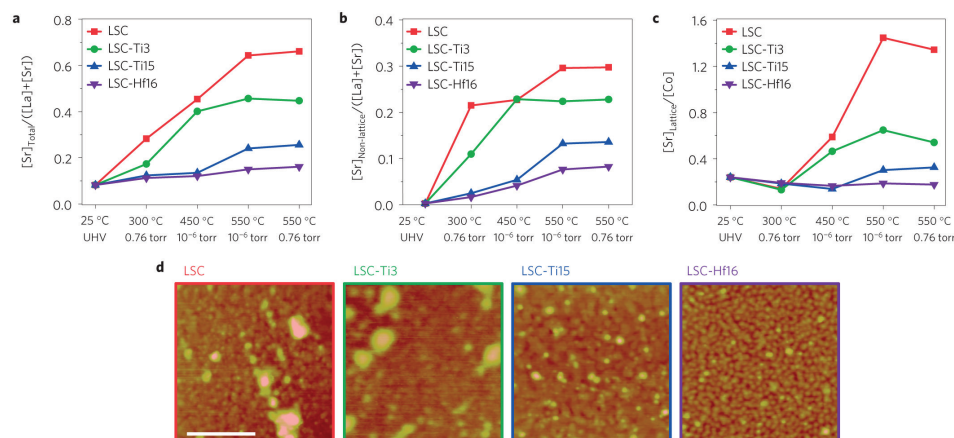
turns into secondary surface phases such as SrO, which blocks the surface electrocatalytic activity. The SOFC community has been working for years to find a workable solution to this problem.

In a previous study, the researchers pinpointed two physical driving forces for

this strontium surface segregation: electrostatic interactions and the minimization of elastic energy. In this work, the group focused on electrostatic interactions at the surface of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (LSC), a state-of-the-art perovskite cathode material with high electrochemical performance. To reduce the concentration of oxygen vacancies, which attract strontium toward the surface through electrostatic attraction, the researchers deposited binary oxides (HfO_2 , TiO_2 , ZrO_2 , and V_2O_5) on the surface at submonolayer coverages, using a feasible chemical bath method. They found that HfO_2 and TiO_2 greatly enhanced the surface stability of LSC against strontium segregation and improved performance by a factor of up to 30.

To test whether they were indeed tuning the surface oxygen vacancy content, the researchers performed AP-XPS and AP-XAS experiments at ALS Beamline 9.3.2. AP-XPS is a novel and powerful materials-characterization tool that can only be found in a few synchrotron beamlines around the world. Traditionally, x-ray photoelectron spectroscopy can only be performed under ultrahigh-vacuum conditions, far from realistic operating conditions for fuel-cell cathode materials. Ambient-pressure studies at the ALS allow the observation of changes in the chemical composition of LSC surfaces in environments close to the operating conditions of SOFC cathodes, providing valuable, meaningful, and operationally relevant results.

At high temperature (550 °C) and high oxygen pressure (0.76 Torr), the AP-XPS data showed that the LSC–Hf sample exhibited the least amount of surface-segregated strontium. Co L-edge and O K-edge XAS as well as valence-band spectra showed that the addition of Hf reduced the concentration of surface oxygen vacancies (missing oxygen sites). This effect largely mitigates the electrostatic driving force of strontium surface



Surface chemical stability on LSC thin films. (a–c) Strontium concentration ratios at the surface measured in situ at different temperatures and oxygen partial pressures by AP-XPS. (d) Ex situ atomic-force microscopy images following the AP-XPS measurements. Scale bar = 400 nm.

segregation, thus greatly improving the stability of LSC surfaces. The results demonstrate that, in an ideal cathode material, a balance must be struck between reactivity and stability, challenging the conventional wisdom that oxygen-vacancy concentration has a solely beneficial effect on electrochemical performance.

The researchers note that this approach is not material specific; they are currently working to apply it to other

perovskite oxide systems. Also, strontium surface segregation is not just an issue for SOFC cathode materials. Other applications, such as thermochemical fuel production, solid-oxide electrolysis cells, and oxygen gas-separation membranes, all suffer from the same issue, albeit under different gas atmospheres. Fundamentally, the aim is to resolve the atomic structure formed on these chemically modified surfaces—something that will need more synchrotron work to accomplish.

Publication about this research: N. Tsvetkov, Q. Lu, L. Sun, E.J. Crumlin, and B. Yildiz, “Improved chemical and electrochemical stability of perovskite oxides with less reducible cations at the surface,” *Nature Materials* **15**, 1010 (2016). doi:10.1038/nmat4659

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