RESNICK INSTITUTE
science + energy + sustainability

RESEARCH HIGHLIGHTS

From the Resnick Sustainability Institute Graduate Research Fellows at the California Institute of Technology

A New Instrument For Characterizing Solid Oxide Fuel Cell Catalysts

Rob Usiskin

In partnership with Ichiro Takeuchi and Shingo Maruyama at the University of Maryland with additional funding provided by the National Science Foundation

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Global Significance

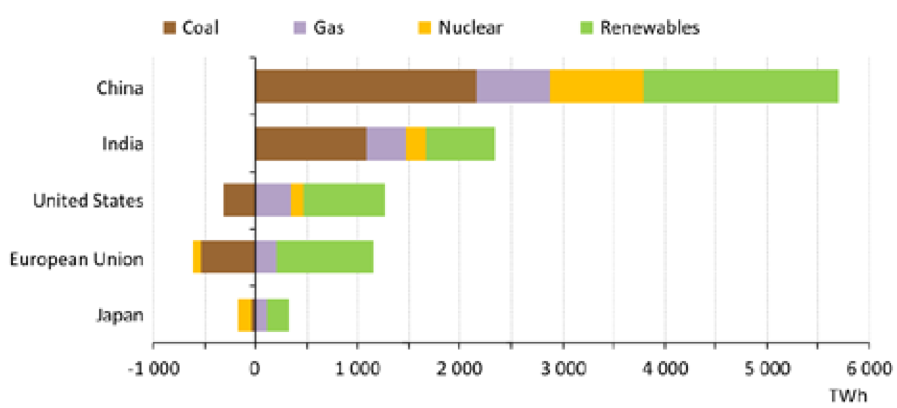
Worldwide demand for electricity is projected to increase by 70% in the next two decades. Meeting this demand in an environmentally sustainable way will require efficient and cost-effective technologies that support a transition from fossil fuels to renewable energy sources.

Solid oxide fuel cells (SOFCs) have enormous potential in this area. **SOFCs are the most efficient devices yet invented for converting fuel into electricity.** Industrial systems that cogenerate electricity and heat using SOFCs have projected efficiencies of up to 75%, far exceeding what is possible in combustion systems. SOFCs are also fuel flexible; they can generate electricity from natural gas, hydrogen, ethanol, propane, biofuels, and more.
From a technological perspective, a commercially viable SOFC device would be an enormous breakthrough.

To date, however, SOFC development has been hampered by inadequate catalyst performance, coupled with a lack of fundamental understanding of how the catalyst can be improved.

To overcome these challenges, this project developed a new instrument for high throughput SOFC catalyst characterization that accelerates our ability to understand existing catalysts and discover new catalysts.

Projected Change in Electricity Generation, 2010-2035



Source: http://www.worldenergyoutlook.org/media/weowebsite/2012/PresentationtoPress.pdf

A New Instrument For Characterizing Solid Oxide Fuel Cell Catalysts

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Project Summary

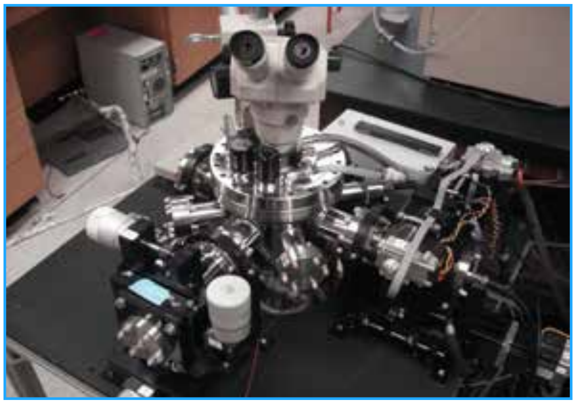
In this project we constructed a unique instrument for measuring the properties of SOFC catalysts: an **automated impedance microprobe.** The instrument is a cross between a kiln, an environmental chamber, and a robot. It heats a sample to the catalyst operating temperature (typically 500˚C - 800˚C), it varies the gas environment in a controlled way, and it uses a precision robotic arm to touch the catalyst with a probe and take detailed measurements of the catalyst properties.

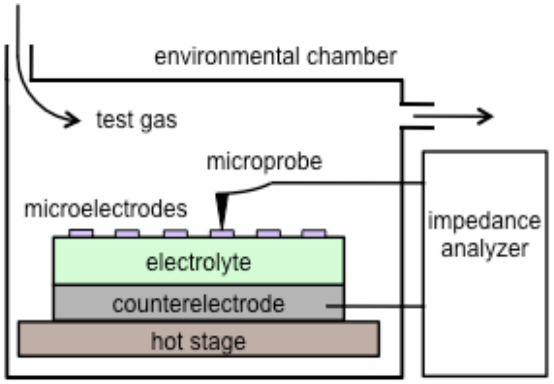
A key aspect of this method is that a single sample can contain an array of hundreds of tiny catalyst "dots", and the geometry and composition of these dots can be systematically varied across the array. In this way a wide range of trends in catalyst properties can be measured, enabling both fundamental studies and new materials discovery. Moreover, by preparing all the dots simultaneously on a single sample, we dramatically increase throughput while avoiding subtle variations in fabrication steps that can occur if multiple samples are used.

This project fuses many disciplines: mechanical engineering (for building the microprobe), materials science (for sample preparation), programming (for automated data acquisition), electrochemistry (for interpreting the data), and more.

Potential Impact

A better understanding of the connection between material properties and SOFC catalyst performance will help us discover better catalysts and optimize their microstructure in a real generator. Our expectation is that this increased performance will enable the generator to operate at lower temperatures, which in turn will make it unnecessary to use expensive high-temperature-compatible alloys in the support components, which will lead to major reductions in cost and greater commercial viability.





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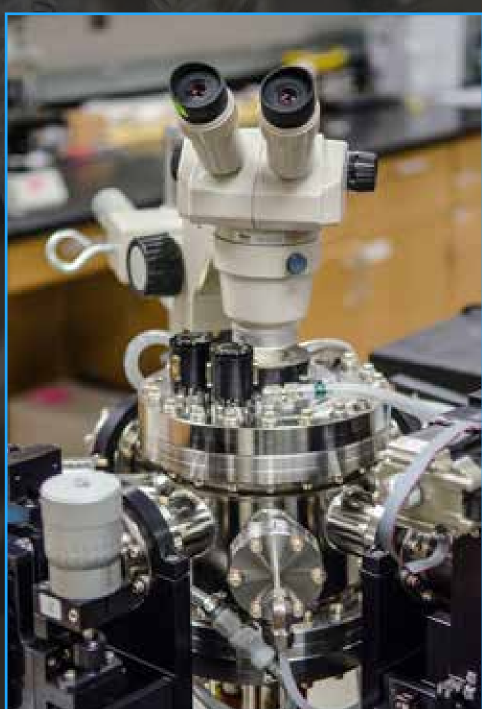
The Science

Inside the impedance microprobe, catalyst films shaped like tiny "dots" with systematically varied dimensions are probed under realistic operating conditions using impedance spectroscopy (a technique that measures sample impedance by applying a small a.c. voltage at various frequencies and dividing by the resulting a.c. current). The resulting impedance spectra are then fitted to extract resistances and capacitances that correspond to different steps in the catalysis. Typically from the resistance values we extract kinetic parameters (e.g., charge transfer rates, diffusion rates), and from the capacitance values we extract thermodynamic parameters (e.g., carrier concentrations, enthalpy of oxidation).

Several advantages are gained because the catalyst dots have small and well-controlled dimensions (diameters as small as 30 um, thicknesses as small as 30 nm). In particular, hundreds of dots can be included in a single sample, allowing high throughput and minimizing errors due to fabrication differences between samples. Also, the dots' tiny size allows us to neglect the counter-electrode impedance in our measurement. In this way, we are able to decouple the anode and cathode processes without using reference electrodes, which historically have been unreliable for systems with solid electrolytes.



Custom automated impedance microprobe developed for this project.

150 dots of ceramic catalyst $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ on a 5 mm x 5 mm substrate

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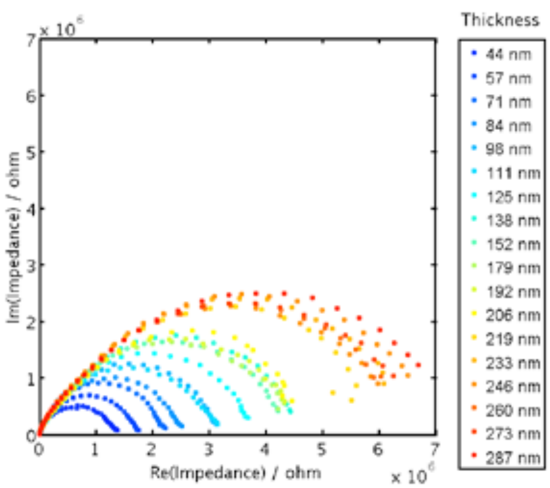
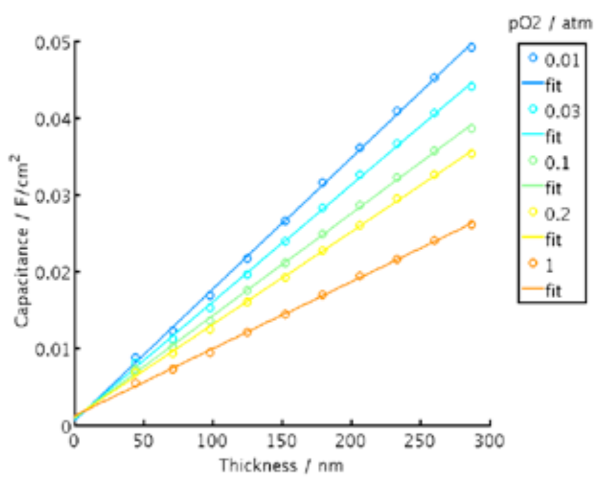
Key Results & Future Steps

Results from two typical sample are shown below. The plot on the left shows raw impedance data corresponding to oxygen reduction ($O_2 + 4e^- \longrightarrow 2O^{2-}$) at 700°C on $La_{0.8}Sr_{0.2}MnO_{3-d}$, also called LSM. LSM is a common SOFC catalyst whose catalysis is commonly thought to occur at edges, in which case thickness would not matter much. Here, however, we see that the impedance increases with increasing dot thickness, suggesting that oxygen ions are diffusing through the dot, and thus that the catalysis is occurring on the top surface of the material, not just at the edges. This observation immediately suggests a different strategy for improving the performance of LSM-based fuel cells: reduce the thickness of the LSM, rather than increasing its edge length.

The plot on the right shows the measured capacitance at 570°C of another common SOFC catalyst, $La_{0.5}Sr_{0.5}CoO_{3-d}$. This total capacitance has bulk and interfacial contributions. We can decouple these contributions by measuring dots with many different thicknesses and then extrapolating to zero thickness, as shown in this plot (the non-zero intercept is the interfacial capacitance). These capacitances are directly related to the bulk and interfacial oxygen vacancy concentrations in the film. The non-zero intercept is the interfacial capacitance; the remaining chemical capacitance is smaller than in bulk samples, implying that the oxygen vacancy concentration changes differently in thin films.



Impedance spectra of $La_{0.8}Sr_{0.2}MnO_{3-d}$ dots with 200 mm diameter at 700°C in C in 100% O_2



Total capacitance of $La_{0.5}Sr_{0.5}CoO_{3-d}$ films at 570°C in

The impedance microprobe is now online and rapidly measuring hundreds of catalyst dots under realistic fuel cell operating conditions, using systematic variations of several experimental variables to quantify fundamental material parameters:

dot thickness ⟶ carrier concentrations, strain effects
dot diameter, gas composition ⟶ catalytic mechanism
temperature ⟶ activation energy
composition ⟶ effect of dopants, activity of new materials

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To date, however, SOFC development has been hampered by inadequate catalyst performance, coupled with a lack of fundamental understanding of how the catalyst can be improved.

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A key aspect of this method is that a single sample can contain an array of hundreds of tiny catalyst "dots", and the geometry and composition of these dots can be systematically varied across the array. Thus a wide range of trends in catalyst properties can be rapidly measured, enabling both fundamental studies and new materials discovery.

The Science

Inside the microprobe, catalyst films shaped like tiny "dots" with systematically varied dimensions are probed under realistic operating conditions using impedance spectroscopy (a technique that measures sample impedance by applying a small a.c. voltage at various frequencies measuring the resulting a.c. current). The resulting impedance spectra are then fitted to extract resistances and capacitances that correspond to different steps in the catalysis. Typically from the resistance values we extract kinetic parameters (e.g., charge transfer rates, diffusion rates), and from the capacitance values we extract thermodynamic parameters (e.g., carrier concentrations, enthalpy of oxidation).

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Key Results

In $La_{0.8}Sr_{0.2}MnO_{3-d}$, a widely used cathode material, oxygen reduction is limited by bulk diffusion under some realistic operating conditions, which suggests an alternative strategy for making better cathodes: minimize the thickness of interfacial features.

In $La_{0.5}Sr_{0.5}CoO_{3-d}$ films, interfacial capacitances are small but non-zero, and the oxygen vacancy concentration changes differently than in bulk samples.