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14. ABSTRACT

Solid electrolytes are highly and increasingly important energy technology components, but high operating temperatures tend to limit their utility. Such temperatures are required, in large part, so that the kinetics of the ion exchange reactions at the surfaces are sufficiently fast. A highly promising means to improve low temperature surface exchange is via mechanical strain. Such effects have been demonstrated in bulk ion diffusion but not, to date, in surface exchange.

In this work, we have created model systems to systematically measure the ability to engineer strain-based

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Final Report: STIR: Improved Electrolyte Surface Exchange via Atomically Strained Surfaces

ABSTRACT

Solid electrolytes are highly and increasingly important energy technology components, but high operating temperatures tend to limit their utility. Such temperatures are required, in large part, so that the kinetics of the ion exchange reactions at the surfaces are sufficiently fast. A highly promising means to improve low temperature surface exchange is via mechanical strain. Such effects have been demonstrated in bulk ion diffusion but not, to date, in surface exchange.

In this work, we have created model systems to systematically measure the ability to engineer strain-based increases in oxygen exchange kinetics of ceramic surfaces using a thin film deposition technique developed at the University of Delaware. Concomitant with the experimental work, we also conducted numerical simulations of the experiments. A Poisson-Nernst-Planck system modified to include reaction terms was built in COMSOL Multiphysics to describe the mass and charge fluxes related to electrons and both neutral and charged oxygen species within the electrode and electrolyte and along all interfaces.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

“Heterogeneous, ion-conducting thin films,” Oxide Thin Films for Advanced Energy & Information Applications, Chicago, IL, Jul. 14, 2014

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

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TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Benjamin McNealy	0.60	
Ning Ye	1.00	
FTE Equivalent:	**1.60**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Joshua L. Hertz	0.00	No
Ajay K. Prasad	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

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This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

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Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

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Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

The key results from our work can be split between the experimental and the computational studies. For the experimental side of this work, YSZ surface films were conclusively demonstrated to support residual stresses based on lattice mismatch with underlying atomic layers. For example, x-ray diffraction results showed that the lattice parameter of YSZ on polished, single crystal sapphire surfaces was consistently dilated to a value of 5.23 Å (from an expected value of 5.14 Å based on measurements of bulk ceramics). This result can be compared to lattice parameter measurements of 5.16 Å for nominally identical films on MgO substrates, a clear demonstration that the films are affected by the underlying lattice. Despite this advance, continued experimental work showed that obtaining usefully engineered lattice dilation and contraction may not be straightforward. Measurements were made of YSZ and ceria films placed on films with zirconia-ceria solid solution compositions engineered to provide varying degrees of lattice mismatch. It was consistently found that ceria films could be compressed, but YSZ films could not be dilated—precisely the opposite of what is likely to be useful in creating faster oxygen exchange kinetics.

In the computational studies, first-principles continuum models of realistic samples were fully implemented and are able to clearly show the dependence of overall device impedance on various surface exchange and bulk parameters (e.g., Figure 1). This result significantly advances our ability to translate experimental impedance spectra into quantitative, physically meaningful values, moving significantly beyond equivalent circuit analysis. Because these models are based on fundamental electrochemistry, the same models have been tweaked with very slight changes in boundary conditions to model the behavior under DC studies with expanded voltage range (e.g., Figure 2) or with chemical in place of electrical driving forces. Thus, the applicability of the results of this study are quite broad. Specific key results soon to be published from this work include that the adsorption rate constant controls the behavior of platinum electrodes on YSZ surfaces much more than the reaction rate constant for charge transfer. A parametric study has placed bounds on the values of these reaction rate constants where each is controlling of the overall sample impedance. This result is significant in light of the well-established difference in performance of platinum electrodes on YSZ vs. on doped ceria surfaces. If it is the adsorption rate that is controlling overall measured behavior, then the improved electrode kinetic behavior must be arising from increased adsorption rate and not increased charge transfer rate on the ceria surface.

Technology Transfer

Final Report

❖ *Statement of the problem studied*

Solid electrolytes are highly and increasingly important energy technology components, but high operating temperatures tend to limit their utility. Such temperatures are required, in large part, so that the kinetics of the electrochemical half-reactions at the surfaces are sufficiently fast. Nearly identical reactions describe the processes occurring on the surfaces of solid oxide fuel cells (SOFCs) and electrolyte cells (SOECs), oxidation/reduction catalysts, oxide-based chemical sensors, and even metals undergoing corrosion. Unfortunately, there has been little fundamental research to date on means to understand and, ultimately, improve these kinetics. A significant reason for this is that ceramic surfaces – even if only the last few atomic layers – are very different from the bulk after the high temperature processing that is required in traditional ceramic fabrication. For example, it has been very well established that dopants and impurities segregate to the surfaces during the high temperature processing that ceramics normally require [1-7]. We have shown that the silicon contaminants found on sintered yttria-stabilized zirconia (YSZ) surfaces leads to exchange rates depressed by up to 3 orders of magnitude [8]. Current studies fabricate and then measure the exchange rate on a surface where the local composition, crystallography, and mechanical strain are effectively uncontrolled. These measurements thus depend on the raw material source and are likely to be highly misrepresentative of the indicated (bulk) composition. To date, no technique has allowed the fabrication of these materials with surface composition controlled at the atomic level, and thus the ability to study surface effects has been extremely limited, with no ability for systematic study.

A highly promising means to improve surface exchange is via mechanical strain. The difference in volume between a vacant and a filled oxygen ion lattice site results in a reaction volume and an associated $V_{ex} \cdot \Delta P$ term in the Arrhenius rate equation. In addition, tensile strain (i.e., negative ΔP) of 1% – 4% is predicted to decrease cation-oxygen bond energy in YSZ and, presumably, other fluorites. For both reasons, tensile strain-based reduction in activation energy is expected to yield exponentially improved ion transport kinetics. Such effects have been demonstrated in bulk ion diffusion but not, to date, in surface exchange. In this work, we have created model systems to systematically measure these phenomena using a film deposition technique developed at the University of Delaware.

Concomitant with the experimental work, we also conducted numerical simulations of the experiments. In recent work at the University of Delaware [9-13], we used finite element solution of generalized Poisson-Nernst-Planck differential equations that govern the behavior of systems with multiple charge carriers. Such systems can be used to directly model the platinum-oxygen-oxide electrolyte system being studied here. A continuum model describing the microelectrode impedance measurements was built using COMSOL MultiPhysics. This software allows the solution of arbitrarily complex systems of partial differential equations on finite element meshes. In this work, a Poisson-Nernst-Planck system modified to include reaction terms was used to describe the mass and charge fluxes related to electrons and both neutral and charged oxygen species within the electrode and electrolyte and along all interfaces.

❖ *Summary of the most important results*

The key results from our work can be split between the experimental and the computational studies. For the experimental side of this work, YSZ surface films were conclusively demonstrated to support residual stresses based on lattice mismatch with underlying atomic layers. For example, x-ray diffraction results showed that the lattice parameter of YSZ on polished, single crystal sapphire surfaces was consistently dilated to a value of 5.23 Å (from an expected value of 5.14 Å based on measurements of bulk ceramics). This result can be compared to lattice parameter measurements of 5.16 Å for nominally identical films on MgO substrates, a clear demonstration that the films are affected by the underlying lattice. Despite this advance, continued experimental work showed that obtaining usefully engineered lattice dilation and contraction may not be straightforward. Measurements were made of YSZ and ceria films placed on films with zirconia-ceria solid solution compositions engineered to provide varying degrees of lattice mismatch. It was consistently found that ceria films could be compressed, but YSZ films could not be dilated—precisely the opposite of what is likely to be useful in creating faster oxygen exchange kinetics.

In the computational studies, first-principles continuum models of realistic samples were fully implemented and are able to clearly show the dependence of overall device impedance on various surface exchange and bulk parameters (e.g., Figure 1). This result significantly advances our ability to translate experimental impedance spectra into quantitative, physically meaningful values, moving significantly beyond equivalent circuit analysis. Because these models are based on fundamental electrochemistry, the same models have been tweaked with very slight changes in boundary conditions to model the behavior under DC studies with expanded voltage range (e.g., Figure 2) or with chemical in place of electrical driving forces. Thus, the applicability of the results of this study are quite broad. Specific key results soon to be published from this work include that the adsorption rate constant controls the behavior of platinum electrodes on YSZ surfaces much more than the reaction rate constant for charge transfer. A parametric study has placed bounds on the values of these reaction rate constants where each is controlling of the overall sample impedance. This result is significant in light of the well-established difference in performance of platinum electrodes on YSZ vs. on doped ceria surfaces. If it is the adsorption rate that is controlling overall measured behavior, then the improved electrode kinetic behavior must be arising from increased adsorption rate and not increased charge transfer rate on the ceria surface.

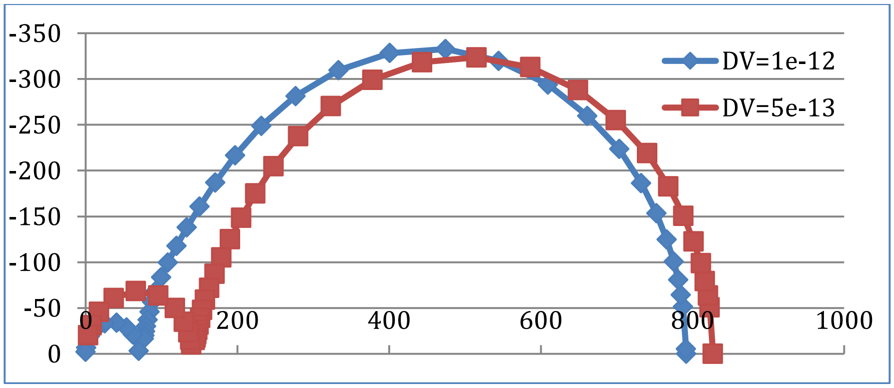

Figure 1. A simulated impedance plot for a 25 µm wide, microelectrode on a thin film YSZ electrolyte with two values of oxygen vacancy diffusivity, showing the measurable change in sample behavior expected. Both the electrolyte impedance (smaller semicircle at left) and the electrode reaction impedance (larger semicircle at right) are affected.

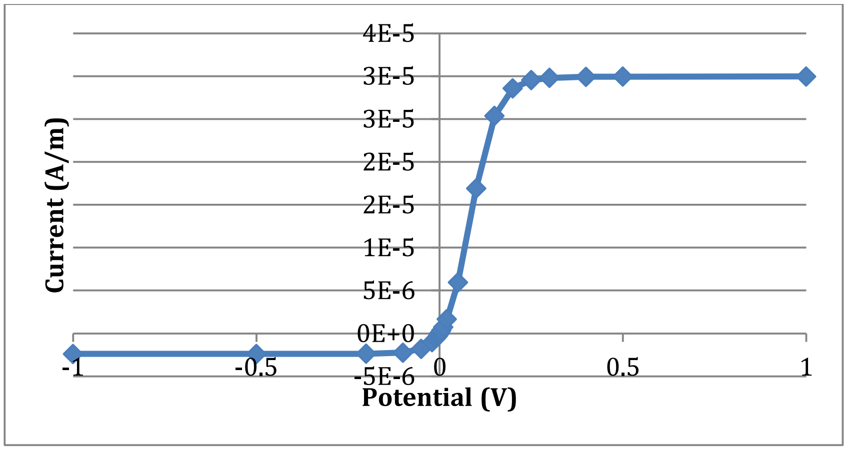

Figure 2. The DC polarization behavior modeled for a similar sample to the one whose impedance spectra are presented in Figure 1. The ability to quickly switch between modeling AC and DC measurement modes is a significant advantage of the models developed in this work.

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