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Organic Solar Cells with Graded Exciton-dissociation Interfaces

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Sponsorship: DOE

With a theoretical efficiency similar to conventional inorganic photovoltaics (PV) and the potential to be manufactured inexpensively over large areas, organic semiconductor technology offers a promising route to ubiquitous solar energy generation [1]. However, despite significant improvements in efficiency in recent years, additional progress is still needed before organic photovoltaics can compete with other photovoltaic technologies [2]. Organic heterojunction PVs suffer from recombination of separated charges at the exciton-dissociation interface [3]. Ultimately, this recombination limits the efficiency of organic PVs. Device structure modifications represent one of the most promising routes to higher efficiency.

In our work, we reduce the recombination of separated electrons and holes at the exciton-dissociation interface by introducing an additional thin interfacial layer sandwiched between the active semiconductor layers. The interfacial layer in this architecture creates a cascade energy structure at the exciton-dissociation interface as shown in the inset of Figure 1. Previous efforts to add

an interfacial layer in organic PVs have suffered due to poor materials selection [4], [5] Reducing recombination losses yields increases in both open circuit voltage (V_{oc}) and short-circuit current (J_{sc}) leading to higher power-conversion efficiencies, as illustrated in Figure 1. We are studying how the energy level alignment of the interfacial layer impacts recombination and developing criteria for optimal interface material design and selection.

As illustrated in Figure 2, we find that devices with too thin an interfacial layer demonstrate limited improvements in charge collection due to partial layer coverage. Conversely, devices with interfacial layers that are too thick suffer from carrier-transport problems in the interfacial layers. Determining the optimal interfacial layer thickness promises to give greater insight into the physical mechanism of charge-carrier recombination at the exciton dissociation interface in organic PVs.

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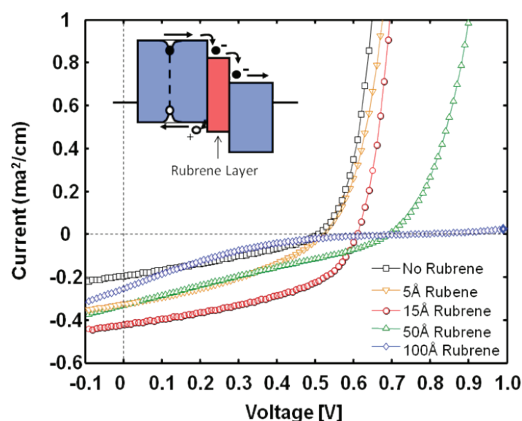


FIGURE 1: Current-Voltage characteristics for devices with and without a Rubrene interfacial layer. Devices with a thin layer of Rubrene at the exciton-dissociation interface exhibit increased short-circuit current and increased open-circuit voltage. However, at large interfacial layer thicknesses, the current decreases.

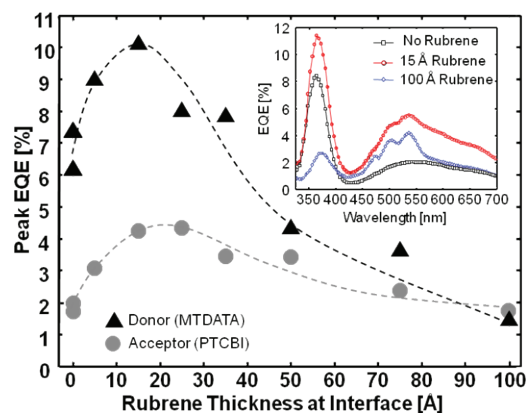


FIGURE 2: Devices with thin interfacial layers exhibit higher external quantum efficiencies. The optimal layer thickness is approximately 15Å. The interfacial layer reduces recombination of separated charges at the exciton-dissociation interface.

Luminescent Solar Concentrators for Energy-harvesting in Displays

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Sponsorship: DOE

We present linearly polarized luminescent solar concentrators (LSCs) optimized for energy-harvesting in displays. Current methods to increase the contrast ratio of displays mostly use combinations of linear polarizers to absorb and dissipate incident light. Incidentally, the polarizers also absorb 50% of the light emitted by the display. The inherently absorptive surface of the display, together with the ever-increasing area of televisions and displays in mobile electronics, makes them interesting candidates for energy-harvesting [1]. In this project, we propose to replace the purely absorptive polarizers in displays with two linearly polarized luminescent concentrators (LSCs) [2] (Figure 1a). Conventional polarizers employ aligned molecules that absorb strongly along the long axis of the molecules or polymer strands (see for instance Figure 1b for aligned Coumarin 6 dye molecules). Our device will introduce into the polarizer light-emitting molecules that re-emit the captured photons into the waveguide. These photons travel to the edges of the waveguide by total internal reflection, whereby they are collected by solar cells. This geometry will allow for the solar cells to be placed only in the frame of the display, leaving the entire front surface available for the display.

Figure 2 shows preliminary results for a linearly polarized LSC based on a rod-shaped dye molecule, Coumarin 6, that is aligned in the plane of the substrate using a nematic-liquid-crystal matrix. As can be observed, the optical quantum-efficiency of these films, defined as the fraction of the photons incident on the face of the waveguide versus the number of photons emitted from the edges, is 30%, limited presently by relatively weak absorption. Another 20% of the photons are emitted from the face of the sample, which might hamper the contrast ratio of a display. We propose to use infrared dyes to circumvent this effect.

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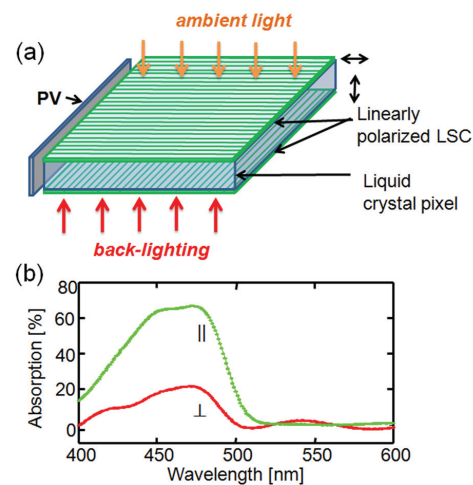


FIGURE 1: (a) A schematic representation of linearly polarized luminescent solar concentrators (LSC) for energy-harvesting in displays. (b) Preliminary results for the absorption of aligned rod-shaped Coumarin 6 dye molecules showing a strong anisotropy between the absorption along the long axis (green) of the molecule and the short axis (red).

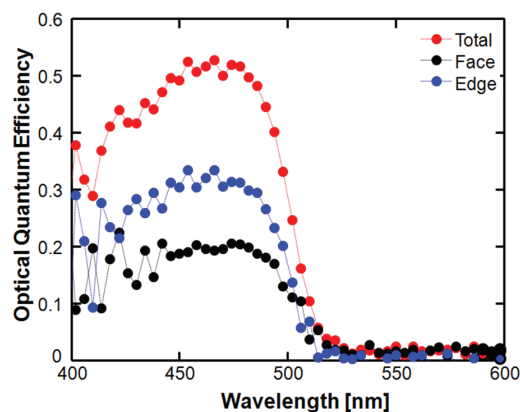


FIGURE 2: The optical quantum efficiency, defined as the fraction of the photons incident on the face of the luminescent concentrator that is emitted from the edge for a linearly aligned system. Only 70% of the incident photons were absorbed for this device.

High-pressure Chemistry: Converting Gases to Liquids for Energy Applications

J. Keybl, K. F. Jensen
Sponsorship: BP

We have designed a microreactor platform to study homogeneous chemical reactions at high temperatures ($<400^{\circ}\text{C}$) and pressures (<100 bar). Microreactor technology has allowed the study of chemical reactions to move from a laboratory-scale batch process to a micro-scale continuous process. This shift leverages the numerous benefits of the micro scale, such as enhanced heat and mass transfer and reduced reactant volumes. Advancements in packaging, coupled with the high mechanical strength of silicon, have allowed these reactions to be carried out at increasingly higher pressures and temperatures. Our microreactor design is based on fabrication principles originally developed for MEMS, specifically lithography, deep reactive ion etching, silicon nitride deposition, and anodic bonding. The microreactor consists of a one-meter-long serpentine $400\text{-}\mu\text{m}$ -wide channel. A halo-etched hole is present to aid thermal isolation between the heated reactor section and the cooled mixing section (see Figure 1). High-pressure fluidic connections are made between the finished microreactor and a stainless steel compression chuck and using silicone o-rings.

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Homogeneous catalyst solutions will be delivered to the microreactor in a liquid solution using a high-pressure syringe pump. Gases such as carbon dioxide or carbon monoxide and hydrogen will be delivered by a second high-pressure syringe pump. They meet at a T-junction within the reactor, forming a two-phase segmented flow regime. Segmented flow is advantageous because it reduces diffusion between adjacent liquid slugs and increases mass transfer between the gas and liquid phases. The completed system has been flow-tested and is able to control temperature to $\pm 0.1^{\circ}\text{C}$ and pressure to ± 0.01 bar at flow rates as small as $5\mu\text{l}/\text{min}$. Extended flow studies were conducted and stable steady-state flows were observed at a variety of conditions within the design envelope (Figure 2). Validation studies using a known gas-to-liquid chemistry are ongoing [1].



FIGURE 1: Silicon microreactor with $400\text{-}\mu\text{m}$ -wide channels. The top half of the reactor is cooled and thermally isolated from the heated bottom half.

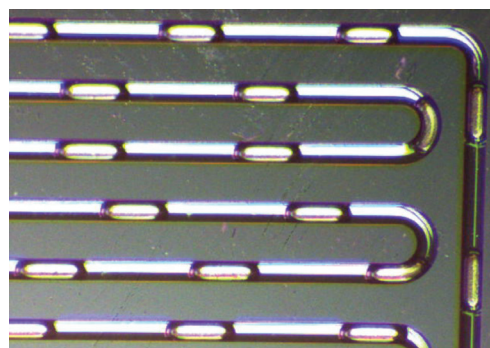


FIGURE 2: Steady segmented flow in the completed system at 40 bar and 105°C . The shorter slugs contain nitrogen gas and the longer slugs contain water.

Nano-engineered Organic Solar-energy-harvesting System

H. W. Lee, S. Bathurst, S.-G. Kim
Sponsorship: KFUPM-MIT Research Program

We envision a new organic photovoltaic cell design: a photo-active layer is positioned in between vertically aligned carbon nanotubes. In an organic solar cell, there are several conversion steps from solar energy to electrical energy, including light absorption, electron-hole pair creation and separation, exciton diffusion, and so on. The power conversion efficiency of an organic photovoltaic cell is much lower than that of silicon-based solar cells [1] since most excitons do not reach at the exciton dissociation site and therefore photon-generated charges are not collected to electrodes efficiently [2].

This research focuses on locating the electron acceptor within an exciton diffusion length from the electron donor by having them distributed at nanometer scale and have a vertically grown CNT array reach them with a 3-dimensional network configuration. To implement the design of well-dispersed electron donor and acceptor materials, we use vertically grown carbon nanotube arrays having 100~150-nm spacing (Figure 1) [3]. Figure 2 shows the conceptual design of our proposed PV device. After growing vertically aligned carbon nanotubes, the SiO₂ dam is structured surrounding the CNT array. Then, the CNT array will be filled with an active polymer layer (a mixture of P₃HT and PCBM) using the thermal inkjet printing method. We expect that our proposed CNT-based organic cell will increase the power-conversion efficiency drastically by collecting the photo-generated charges before they recombine.

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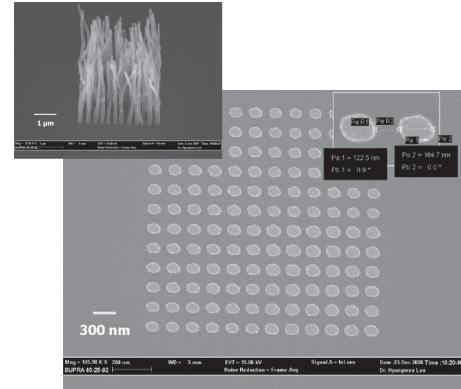


FIGURE 1: An array of catalyst nano dots having 100~150 nm spacing and vertically aligned carbon nanotubes grown by plasma enhanced chemical vapor deposition (PECVD).

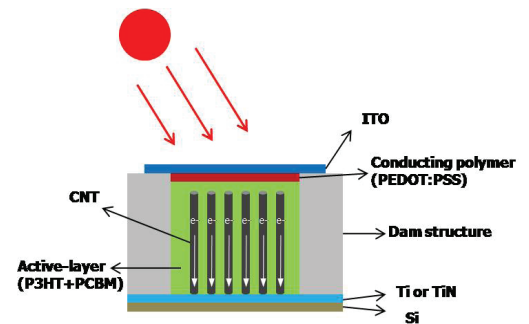


FIGURE 2: The conceptual design of the proposed photovoltaic cell having vertically aligned carbon nanotubes.

Design of Coreless Magnetics for VHF Power Conversion

A. D. Sagneri, D. J. Perreault
Sponsorship: National Semiconductor Corporation, CICS

The desire for power converters with reduced size, weight, and cost has led to an effort to reduce energy storage requirements by switching in the VHF regime (30-300 MHz). At these frequencies, batch-fabricated converters with co-packaged passive components seem nearly within reach. It has already been demonstrated through layout optimization techniques that LDMOSFETs in a standard power process can operate effectively in VHF power converters [1-3]. This work looks at coreless magnetic components with form factors suitable to co-package with a monolithic IC implementing the switching and control functions of a VHF power converter.

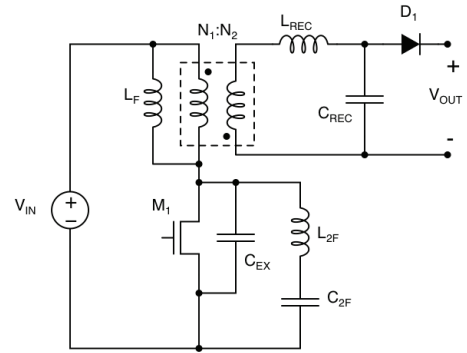


FIGURE 1: The isolated F2 DC-DC converter topology is suitable for use at VHF. The ideal transformer is implemented by a real structure that absorbs L_p as the magnetizing inductance and L_{REC} as leakage inductance to reduce the component count.

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Figure 1 shows an isolated VHF converter topology that requires a transformer and several inductors. The inductors L_F and L_{REC} can be absorbed into the transformer structure to reduce the component count, which eases the mechanics of co-packaging. Absorbing the inductors fixes the inductance matrix description of the transformer. A large number of transformer geometries can realize a given inductance matrix. The goal is to find one that has the best efficiency vs. volume characteristics.

While it is relatively easy to analyze a structure for its inductance matrix, inverting the problem is difficult. Here we first constrain the design space to a planar transformer. It is then possible to use models for the mutual inductance between concentric rings [4] to find a locus of geometries that have approximately the desired inductance characteristics. Each structure is then analyzed using FastHenry [5], to extract the self- and mutual-resistance terms. The full set of transformer parameters is then used to calculate power loss for the desired converter application, yielding a loss-diameter curve from which the desired structure can be picked.

Using this technique, structures are realized (Figure 2) from 4.5 – 10 mm in diameter and 0.8 mm thick. They yield efficiencies from 85% - 93% while transmitting 9.5 W.

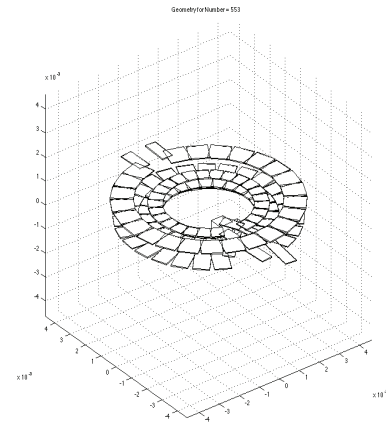


FIGURE 2: A segmented representation of a planar transformer. The transformers are fabricated on a 4-layer 0.031" PCB. Each turn is on a separate layer, so the total number of turns (primary and secondary) is 4.

Solar Thermoelectrics

R. Amatya, R. J. Ram
Sponsorship: MITEI

Solar thermoelectric generators (STG) (Figure 1) employing light concentrators and high-ZT thermoelectric materials are an attractive alternative to solar photovoltaics for micro-power applications. Earlier work on STG [1-3] has shown low system efficiency (<1%) primarily due to small-module ZT and low solar concentration. To date, the highest measured efficiency for solar thermoelectrics is 3.35%, using a unicouple of $ZT = 0.4$ and solar concentration of 50 suns (1 sun = $1000\text{W}/\text{m}^2$) [1]. A low-cost parabolic concentrator can give up to 10 suns of solar radiation. A cost model was developed using a simulation tool called HOMER. Our economic model for a micro-power STG ($\eta_{\text{sys}} \sim 4.5\%$) shows a 30% cost reduction compared to commercial photovoltaics.

A complete thermodynamic analysis based on energy balance and heat transfer allows us to predict system efficiency at any given solar radiation for the STG. The total efficiency depends on both the solar concentrator and the thermoelectric module performance. The concentrator efficiency decreases due to convective and radiative losses from the hot side. Convective losses can be reduced by introducing suppression mechanisms such as multiple glass panels and dead air in between the glass and the absorber. For radiative loss suppression, a special coating called "selective surface" can be utilized; it has larger absorption coefficient at the visible wavelength range and low emissivity at higher wavelengths, where the black body radiation occurs. STG performance is modeled using mature thermoelectric materials such as micro-alloy Bi_2Te_3 and SiGe, as well as novel materials with high material ZT such as ErAs: InGaAlAs and $(\text{AgSbTe})_x(\text{PbSnTe})_{1-x}$ - LAST. At low temperature (< 500K), with Bi_2Te_3 ($ZT_{\text{module}} = 0.77$), η_{sys} of 3.76% can be achieved using air convection at the cold side. At larger temperature range, using selective surface coating and water convection, η_{sys} of 5.5% can be achieved (Figure 2).

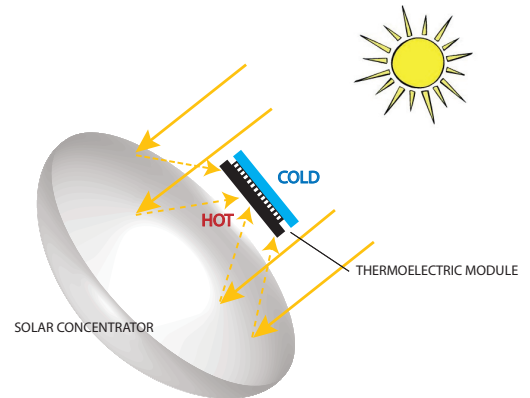


FIGURE 1: Solar thermoelectric generator (STG).

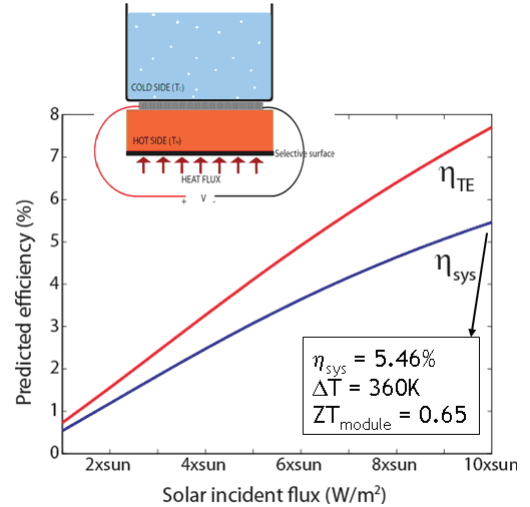


FIGURE 2: Theoretical prediction for module (η_{TE}) and system (η_{sys}) efficiency for a STG using n-type ErAs: InGaAlAs and p-type LAST material.

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Microfabricated Thin-film Electrodes for Solid Oxide Fuel Cells

W. C. Jung, K. Haga, D. Chen, H. L. Tuller
Sponsorship: NSF, DMR-0243993; Saint Gobain

Micro- solid oxide fuel cells (SOFCs) are currently under intense investigation for portable power applications, such as notebook computers and mobile phones [1]. In this work, thin film $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ (STF) cathodes were fabricated on top of single-crystal yttria-doped zirconia (YSZ) solid electrolyte substrate by both pulsed laser deposition (PLD) and thermal inkjet printing (TIJ) (see Figure 1), and their properties were systematically investigated in relation to the cathodic performance of the STF. Various additives were added to the inks to control viscosity and reduce clogging. Deposition conditions were carefully selected to obtain uniform and crack-free films (see Figure 2).

exchange kinetics. Ink jet deposited films were found to exhibit similar performance to PLD-deposited films as long as care was taken that no reaction products between STF and YSZ were formed during sintering.

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Analysis of the impedance spectra, collected on symmetrical cells of the type STF/YSZ/STF over the temperature range of 570 – 650°C and the pO_2 range of 2×10^{-5} – 1 atm, was consistent with the mixed ionic-electronic behavior of the STF characterized by fast surface-oxygen exchange kinetics. Present studies focus on correlating the bulk transport properties of STF with changes in the corresponding changes in oxygen

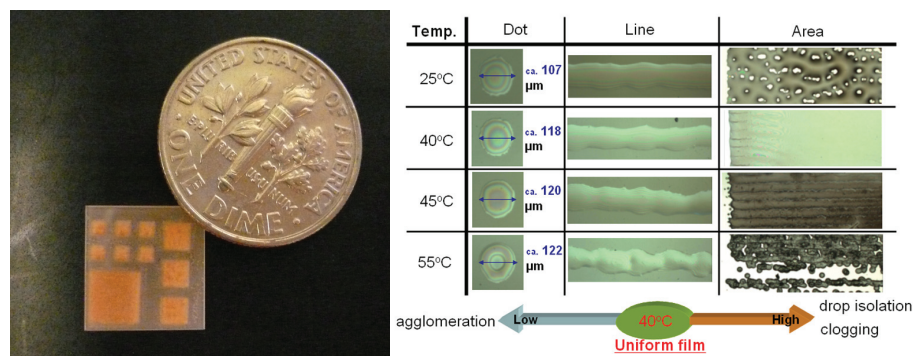


FIGURE 1: A photograph of STF (left) films prepared by thermal inkjet printing and subsequent sintering and (right) the effect of substrate temperature on morphology of ink-jetted STF films.

Thin-film Epitaxial Catalysts for Low-temperature Solid Oxide Fuel Cells

G. J. Ia O', S. J. Ahn, E. C. Crumlin, Y. Shao-Horn
Sponsorship: NSF

A key issue for the commercialization of solid oxide fuel cells (SOFCs) has been the catalytic limitations of the perovskite (ABO_3) cathode (i.e., such as $LaMnO_3$ or $LaCoO_3$) where oxygen reduction reactions (ORRs) occur. The conventional strategy to improve cathode ORR activity has been to synthesize ABO_3 materials with higher oxygen vacancy concentration. This goal has been traditionally accomplished by doping the perovskite A and B sites with aliovalent alkaline-earth (i.e., Sr, Ba, Ca) and transition metal (i.e., Ni, Fe) elements, respectively. Recently, strain-engineered electrode [1] and electrolyte [2] materials for SOFCs have demonstrated remarkable effects on catalytic activity and oxygen ion transport. These effects had been attributed to compressive or expansive strains in the crystal as a result of lattice-mismatched epitaxial growth. Here we report strain-induced catalytic enhancement for ORR on epitaxial (001) $La_{0.8}Sr_{0.2}CoO_3$ (LSC) grown on Y_2O_3 -stabilized

ZrO_2 with Gd_2O_3 -doped CeO_2 buffer layer. In-plane expansive strains of 1.4 % and 0.29 % were observed for 45-nm and 130-nm epitaxial LSC films, respectively, as shown in Figure 1a. These expansive strains resulted in higher oxygen nonstoichiometry for epitaxial LSC films in comparison to bulk LSC, as shown in Figure 1b. Consequently, $\sim 10\times$ higher chemical surface oxygen exchange kinetics (k_{chem}) than bulk LSC [3] were observed for these epitaxial LSC films, as shown in Figure 1c. This study demonstrates a new approach to significantly enhance the catalytic activity of conventional perovskite materials by strain-engineering.

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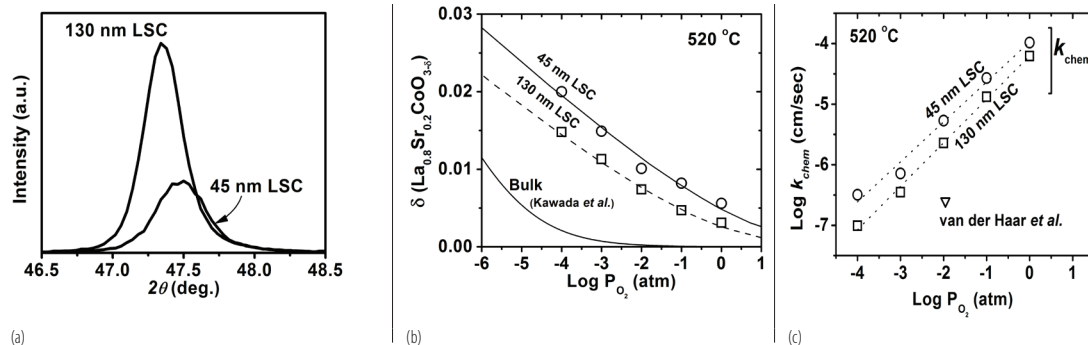


FIGURE 1: (a) Out-of-plane XRD results from LSC (002) reflection with 130-nm LSC peak shifted to a 2θ lower angle indicating relaxation of the strain in the LSC film. (b) Enhanced oxygen nonstoichiometry (δ) for 45-nm and 130-nm LSC films in comparison to bulk LSC [3]. (c) Enhanced k_{chem} for epitaxial films with thickness of 45 nm and 130 nm, in comparison to bulk values previously reported [4].

Microfabricated Thin-film Electrolytes and Electrodes for Solid Oxide Fuel Cells

S. J. Litzelman, W. C. Jung, H. L. Tuller
Sponsorship: NSF

Micro-solid oxide fuel cells (SOFCs) are currently under intense investigation for portable power applications, such as notebook computers and mobile phones [1]. While thin film nanostructured solid electrolytes result in lower cell losses due to reduced ohmic resistance, grain boundaries may serve as fast diffusion pathways for cations, resulting in reduced long-term stability. The effects of grain boundary chemistry and interdiffusion on ionic transport have yet to be systematically investigated.

To explore the relationship between performance and stability, CeO_2 thin films were grown by pulsed laser deposition (PLD) [1] and Ni and Gd were subsequently in-diffused along the grain boundaries in the temperature range of 700-800°C. Novel electron-blocking microelectrodes, prepared via a photolithographic lift-off process, enabled determination of the partial electronic and ionic contributions to the total conductivity. Changes in space charge carrier profiles were modeled to account for changes in carrier transport parallel and perpendicular to the columnar grain boundaries in the CeO_2 film.

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Advanced Photoelectrodes for Photo-assisted Water Electrolysis

J. Engel, H. L. Tuller in collaboration with D. Nocera
Sponsorship: Chesonis Family Foundation

With continuously growing energy demands, new alternative energy solutions become essential. In order to achieve sustainability, efficient conversion and storage of solar energy are imperative [1], [2]. Photoelectrolysis utilizes solar energy to evolve hydrogen and oxygen from water, thereby enabling energy storage via chemical means. This work investigates photoelectrodes, which offer high conversion efficiency, long-term stability, and low cost. The focus is initially on semiconducting metal oxides in which the energy band, defect, and micro-structure are tuned to optimize optical absorption, charge transport and reduced overpotentials.

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