Energy: Photovoltaics, Energy Harvesting, Energy Storage, Fuel Cells

Improving Photovoltaic Conversion Using Spectral Conversion

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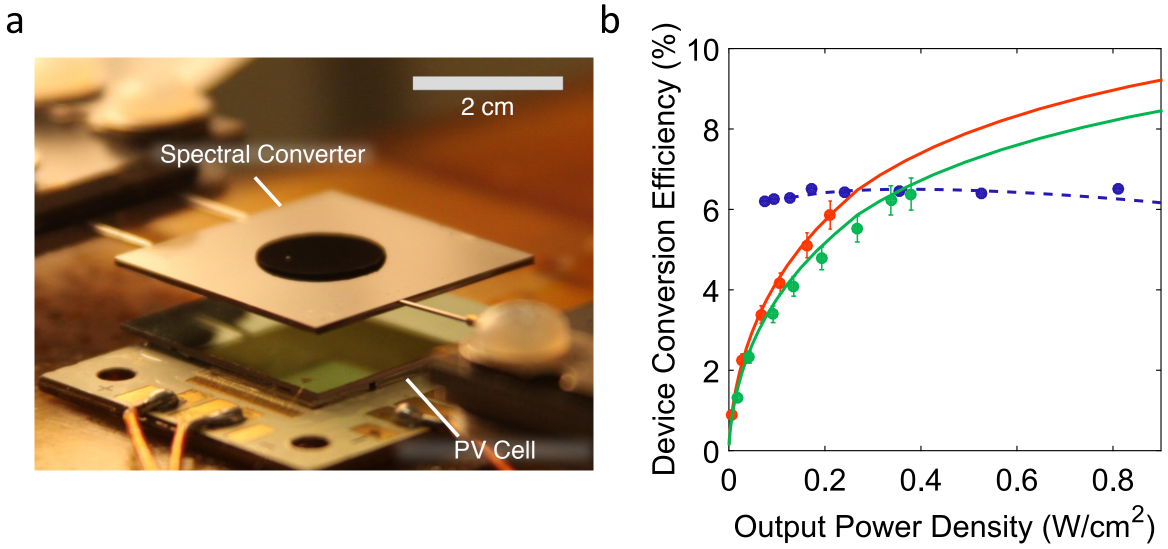
Sponsorship: S3TEC, DOE

A single-junction PV cell generating electrical power through incident sunlight is limited by the Shockley-Queisser limit, which for any bandgap is far below the limiting efficiency of converting work from sunlight. By introducing an intermediate component that absorbs sunlight and re-emits a tailored thermal radiation spectrum towards a single junction PV cell, solar thermophotovoltaics (STPVs) promise to bridge the gap between these two disparate limits.

For STPVs to succeed, a detailed understanding of the energy flow via radiation and heat conduction is key. We have been working to enhance the performance of a single-junction PV by incorporating a spectral converter. The spectral converter consists of a multi-walled carbon nanotube (MW-CNT) area for complete thermalization of incident sunlight, a one-dimensional Si/SiO_2 photonic crystal for spectrally selective thermal emission, and a tandem rugate/interference filter. The PV cell used in the study is a low-bandgap InGaAsSb (E_g = 0.55 eV) cell.

While absolute efficiencies are still low relative to more mature technologies, our peak measured efficiency of 6.8% is above all others reported for STPVs. We have shown improved device conversion efficiency as well as reduced parasitic heat generation as a result of the spectral converter. This is the first time that the performance at the device level of a single junction PV cell has been enhanced due to the presence of a spectral converter.



▲ Figure 1: (a) Optical image of STPV device. Top surface has small MW-CNT area for photon absorption and tungsten-coated surface to reduce heat loss through thermal emission. Bottom surface (not shown) produces spectrally selective thermal emission spectrum through one-dimensional photonic crystal and rugate/interference filter. (b) Performance of device shows that STPVs can enhance performance of PV cell by introducing intermediate absorption/re-emission process.

FURTHER READING

- W. Shockley and H. J. Queisser, "Detailed Balance Limit of Efficiency of P-N Junction Solar Cells," *Journal of Appl. Phys.*, vol. 32 no. 3, pp. 510, 1961.
- P. Würfel and U. Würfel, *Physics of Solar Cells: From Basic Principles to Advanced Concepts*, Hoboken: John Wiley & Sons, 2009.

Oxidative Chemical Vapor Deposition of Polymers for Printable and Flexible Photovoltaics

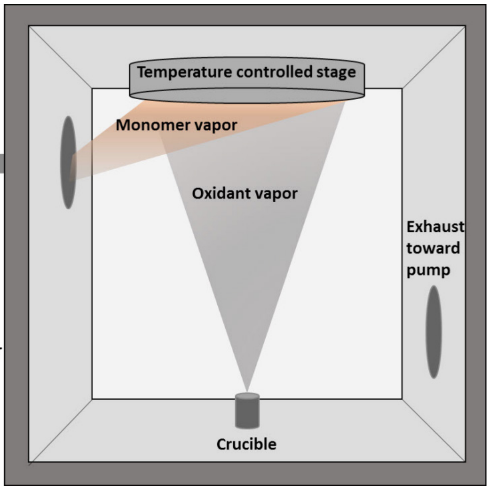
W. J. Jo, K. K. Gleason

Sponsorship: Eni S.p.A, Samsung Electronics, Institute for Soldier Nanotechnologies

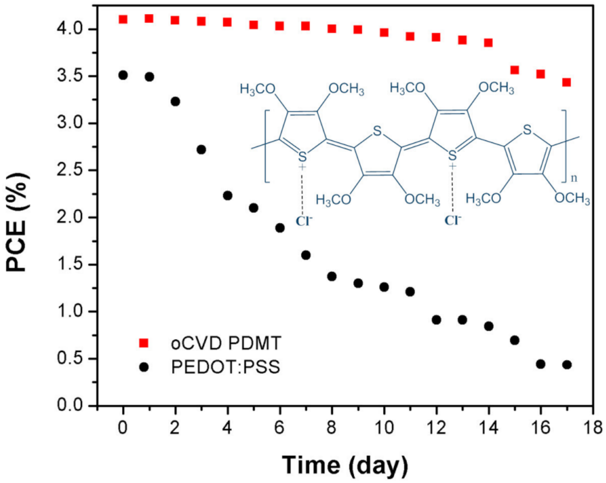
A variety of solar energy conversion systems has emerged as attractive candidates to establish fossil fuel-free energy networks. Among these, organic solar cells offer the promise of a lightweight, flexible, large-area, and cost-effective photovoltaic technology. Traditionally, organic photovoltaic devices (OPVs) have been fabricated with thermal evaporation or solution-based techniques, but these two methods are suitable for only low molecular weight or soluble materials. In order to apply high molecular weight and insoluble polymers to OPVs, we explore the use of oxidative vapor deposition (oCVD) for the polymer deposition.

As Figure 1 shows, oCVD is a solvent-free conformal vacuum-based technique to enable thin-film fabrication of insoluble polymers at moderate vacuum (~ 0.1 Torr) and low temperature (25–150˚C). Moreover, oCVD carries the well-cited processing benefits of vacuum processing, such as parallel and sequential deposition, well-defined thickness control, large-area uniformity, and inline integration with other standard vacuum processes (e.g., vacuum thermal evaporation).

Based on the aforementioned technical advantages from oCVD, various insoluble polymers are successfully applied to OPVs. First, polyselenophene donor layers are integrated into OPVs for the first time with 0.4 % of power conversion efficiency. Second, ternary OPVs employing polythiophene donor layers has been realized to increase the power conversion efficiency up to 2.4%. Third, a new concept of neutral hole transporting layers (HTLs) is achieved by integrating patterned Cl^-doped poly(3,4-dimethoxy-thiophene) (PDMT) HTLs into OPVs via oCVD. Due to this novel polymer's neutrality, high transparency, good conductivity, and appropriate energy levels, the power conversion efficiency and lifetime of OPVs are remarkably boosted compared to those of OPVs depending on the commercial hole transporting polymer, acidic PEDOT:PSS [poly(3,4-ethylenedioxythiophene):polystyrene sulfonate] (Figure 2). Finally, we are currently studying hyper-conductive PEDOT for printable and flexible electronics by using a vacuum-based polymer vapor printing technique – oxidative chemical vapor deposition (oCVD) combined with *in situ* shadow masking.



▲Figure 1: Schematic of oCVD reactor.



▲Figure 2: Evolution of power conversion efficiency with respect to storage time under N_2 atmosphere.

FURTHER READING

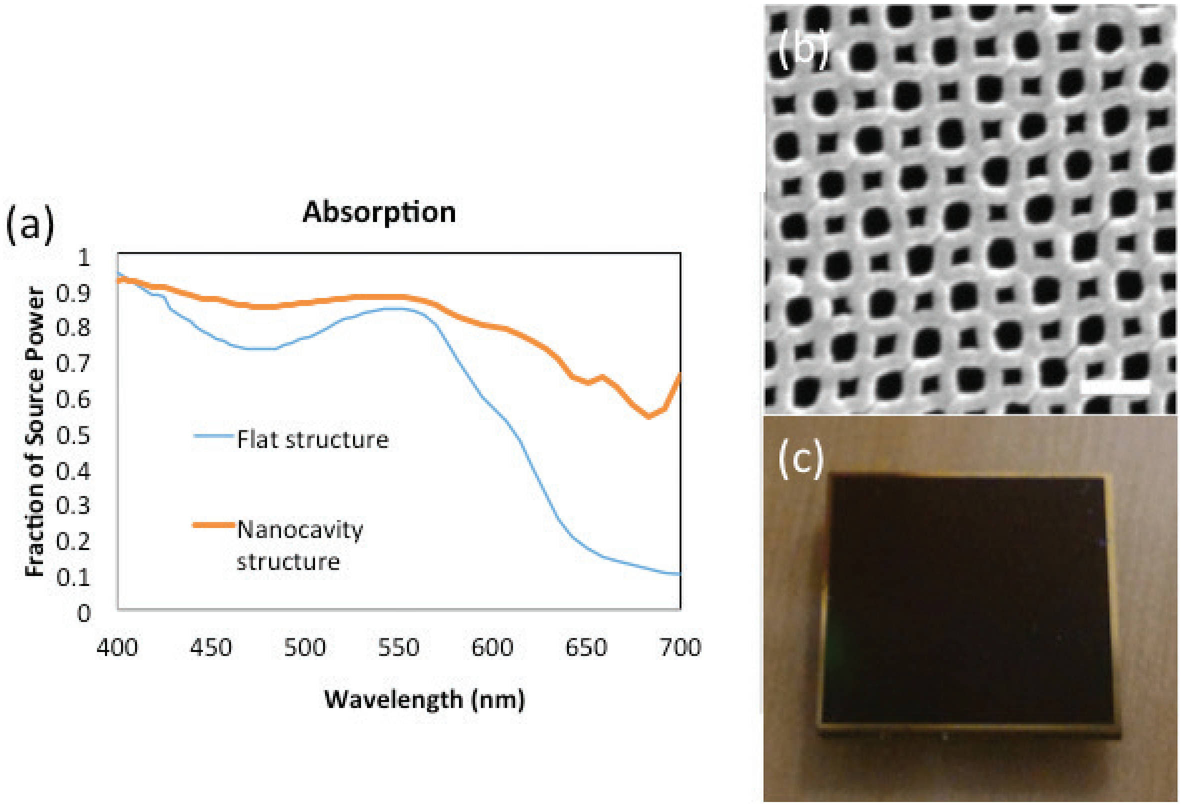
- W. J. Jo, J. T. Nelson, S. Chang, V. Bulović, S. Gradečak, M. S. Strano, and K. K. Gleason, "Oxidative Chemical Vapor Deposition of Neutral Hole Transporting Polymer for Enhanced Solar Cell Efficiency and Lifetime," Advanced Materials, 2016.
- W. J. Jo, D. C. Borrelli, V. Bulović, and K. K. Gleason, "Photovoltaic Effect by Vapor-Printed Polyselenophene," *Organic Electronics*, vol. 26, pp. 55-60, 2015.

High-Efficiency Photovoltaic Devices using Nanocavity Array

W. L. Kwan, A. El-Faer, X. Li, S.-G. Kim
Sponsorship: SUTD-MIT Program

We have demonstrated in our earlier results that metal-dielectric nanocavity arrays can improve broad-band light absorption due to the enhancement in the cavity, waveguide, and surface plasma polariton resonance modes around the nanocavity. This project aims to utilize this absorber structure for applications in photovoltaic devices with soft absorber materials like organic and perovskite materials, which have limited carrier lifetime and thereby require ultra-thin film thickness for efficiency charge extraction. However, light absorption is insufficient if the absorber layer is too thin, and a compromise between complete light absorption and charge extraction is often needed, resulting in mediocre energy harvesting efficiencies.

The nanocavity array we fabricated can alleviate the need for thicker absorber film by enhancing broad-band absorption in the absorber material. Figure 1(a) shows the results of a finite-difference time-domain (FDTD) simulation that the absorption in a poly(3-hexylthiophene-2,5-diyl):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) film is enhanced by the nanocavity structure (SEM image in Figure 1(b)). The enhanced absorption can also be clearly seen in the photograph of a thin gold film deposited on the nanocavity array in Figure 1(c). Most of the visible light is absorbed, leaving a black appearance on the surface of the substrate. A prototype device is under fabrication to demonstrate higher solar energy harvesting efficiency.



▲Figure 1: (a) FDTD simulation results on the absorption spectrum of P3HT:PCBM films on a flat surface and nanocavity structure. (b) SEM image of Al_2O_3 nanocavity array coated with gold. The scale bar is 1mm. (c) Photograph of a silicon substrate with Al_2O_3 nanocavity array coated with gold.

FURTHER READING

- J. B. Chou, D. P. Fenning, Y. Wang, M. A. M. Polanco, J. Hwang, A. EI-Faer, F. Sammoura, J. Viegas, M. Rasras, A. M. Kolpakl, Y. Shao-Hom, and S.-G. Kim, "Broadband Photoelectric Hot Carrier Collection with Wafer-scale Metallic-semiconductor Photonic Crystals," *42nd IEEE Photovoltaic Specialist Conference (PVSC),* New Orleans, LA, *2015.*

Germanium-on-Silicon Heteroepitaxy for High-Efficiency Photovoltaic Devices

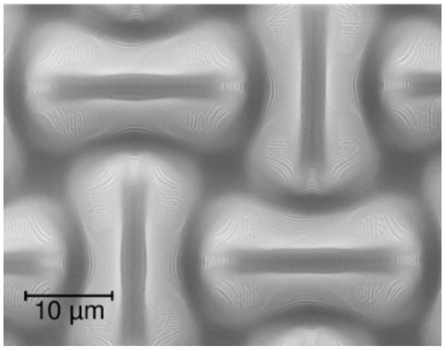
B. R. Albert, L. C. Kimerling, J. Michel

Sponsorship: ARPA-E

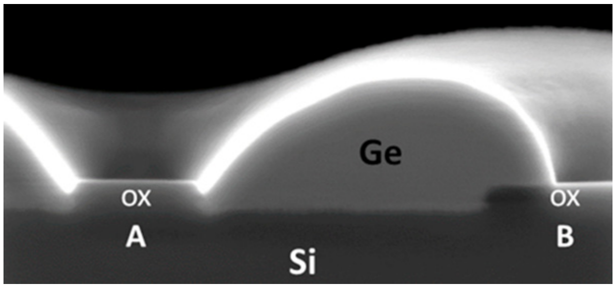
While III-V based photovoltaic cells demonstrate high energy-conversion efficiencies, their widespread adoption is limited by the prohibitive cost per device area. Substantial cost reduction of germanium lattice-matched III-V cells can be realized by replacement of the Ge substrate with a thin layer of Ge deposited on silicon. To maintain efficient energy conversion, the Ge-on-Si "virtual substrate" must be single crystalline with a threading dislocation density (TDD) low enough to not affect carrier lifetimes in the epitaxially deposited III-V layers.

Lateral overgrowth and film coalescence create a more suitable, planar Ge film for III-V growth in large areas. Fabrication of a continuous Ge surface from a patterned Ge film demands complete coalescence during lateral overgrowth. Due to the high surface energy of the Ge/SiO_2 interface, lateral overgrowth does not readily occur. Ge mesa arrays were staggered to eliminate regions entirely dependent on overgrowth from mesa corners. A staggered arrangement decreased the growth time until complete coalescence by at least 50% as compared to a regular gridded array. The rate of overgrowth over isolated SiO_2 lines was observed to increase for smaller line widths up to 1.5 µm.

Etch pit studies of coalesced structures employing faceted Ge growth around SiO_2 walls arranged as grids and isolated lines indicated a local increase in the TDD in the vicinity of Ge film edges while decreasing to 1 x 10^7 cm^{-2} further away in the film. A significant improvement in TDD reduction by avoidance of dislocation pile-up is expected by these same models if blanket Ge is instead grown, followed by etching and filling of trenches with poly-Ge separated by a thin layer of SiO_2. A 1-µm thick Ge film is expected to exhibit a TDD of 1 x 10^5 cm^{-2}. At this density level, the performance of high-efficiency III-V photovoltaic cells will be unaffected.



▲Figure 1: Ge lateral overgrowth over SiO_2 isolated walls.



▲Figure 2: Overgrowth at zero and negative concavity Ge film perimeters.

Solid-State Infrared-to-Visible Upconversion Sensitized by Colloidal Nanocrystals

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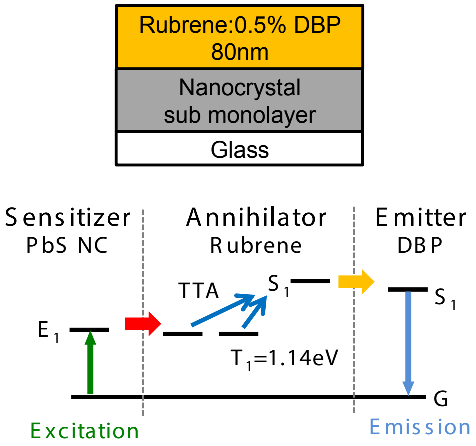
Sponsorship: EFRC Center for Excitonics

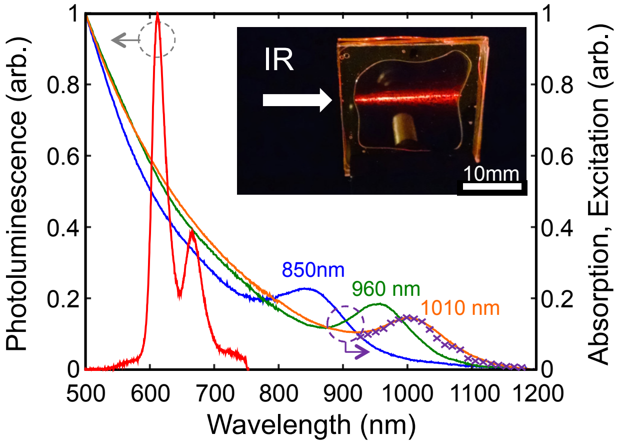
Optical upconversion is a process that converts two or more low-energy photons into a single high-energy photon. Upconversion from the infrared to the visible is useful in photovoltaics, photodetection, bioimaging and three-dimensional displays. In photovoltaic applications specifically, an optical upconversion layer can capture sub-bandgap photons, increasing the efficiency of a conventional single-junction solar cell beyond the Shockley–Queisser limit.

To upconvert light at relatively low intensities, a promising approach is the sensitized triplet-triplet annihilation (TTA). It utilizes a sensitizer and an annihilator. The sensitizer absorbs incident light and transfers the energy as spin-triplet excitons to the annihilator. When two triplets meet in the annihilator, they form a single higher-energy spin-singlet exciton via TTA. Blue-shifted light is emitted when the singlets relax. It has been, however, difficult to identify effective molecular sensitizers that absorb in the infrared. Efficient demonstrations to date have been mostly conversion among visible wavelengths. Furthermore, the majority of them are in solution, while a solid-state architecture is necessary for solar and detection applications.

Here, we report a solid-state thin film for infrared-to-visible upconversion that employs lead sulfide colloidal nanocrystals as a sensitizer; see Figure 1. Upconversion is achieved from pump wavelengths beyond λ = 1 µm to emission at λ = 610 nm (Figure 2). When excited at λ = 808 nm, two excitons in the sensitizer are converted into one higher energy state in the emitter at a yield of 1.2±0.2%. Upconversion efficiency reaches the maximum at an absorbed intensity equivalent to less than one sun. We demonstrate that colloidal nanocrystals are an attractive alternative to existing molecular sensitizers, given their small exchange splitting, wide wavelength tunability and broadband infrared absorption. This solid-state architecture for upconversion may prove useful for enhancing the capabilities of solar cells and photodetectors.



▲ Figure 1: Thin-film device structure (top) and energy diagram (bottom) illustrating TTA-based upconversion sensitized by PbS colloidal nanocrystals (NC). DBP: dibenzotetraphenylperiflanthene.



▲ Figure 2: Nanocrystal absorption labeled by first excitonic peaks, DBP photoluminescence (red), and excitation spectra (purple crosses) for λ=1010nm NC. Inset: photograph of a device under λ=808nm excitation.

FURTHER READING

- M. Wu, D. N. Congreve, M. W. B. Wilson, T. Van Voorhis, V. Bulović, M. G. Bawendi, M. A. Baldo *et al*, "Solid-State Infrared-to-Visible Upconversion Sensitized by Colloidal Nanocrystals," *Nature Photonics*, vol. 10, pp. 31-34, 2016.
- T. N. Singh-Rachford and F. N. Castellano, "Photon Upconversion Based on Sensitized Triplet-Triplet Annihilation," *Coordination Chemistry Reviews*, vol. 254, pp. 2560-2573, 2010.
- T. F. Schulze and T. W. Schmidt, "Photochemical Upconversion: Present Status and Prospects for Its Application to Solar Energy Conversion," *Energy & Environmental Science*, vol. 8, pp. 103-125, 2015.

Solar Water Splitting with Metallic-Semiconductor Photonic Crystals

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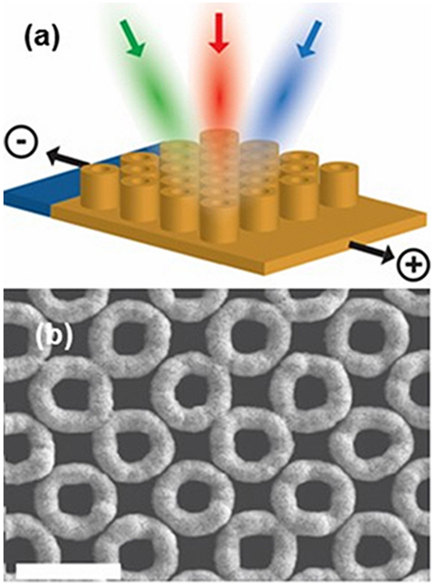
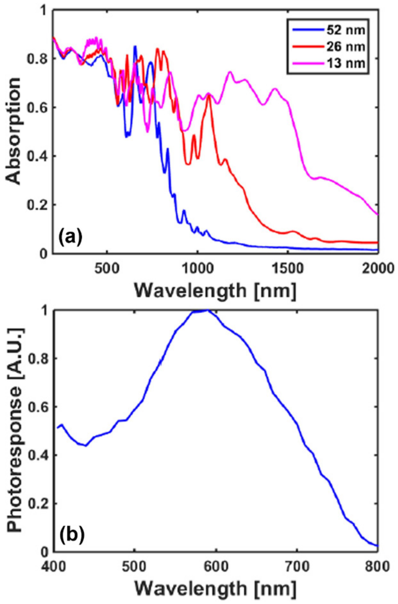
Sponsorship: Masdar Flagship Program

The major challenges for current solar energy harvesting techniques are the limitations in high-efficiency energy conversion and large-scale energy storage. Directly converting solar energy into storable chemical fuels can solve these problems. A promising method is utilizing photoelectric hot electron generation to split water and produce hydrogen fuel. Titanium-oxide-based photocatalytic systems have been widely used in photon-driven hot electron generation. However, the efficiency of the present design is limited due to the low absorption of visible light. Here we report hot electron collection by wafer-scale Au/TiO_2 metallic-semiconductor photonic crystals (MSPhC), with a broadband photoresponse below the bandgap of TiO_2. Multiple absorption modes supported by the 2D micro-cavity structure of the MSPhC extend the photon-metal interaction time and fulfill broadband light absorption. Surface plasmon absorption mode gives access to enhanced electric field oscillation and hot electron generation at the interface between Au and TiO_2. As demonstrated in Figure 1a, the generated hot electrons with enough energy to overcome the Au/TiO_2 Schottky barrier could be collected for water splitting.

Figure 1b shows the micro-cavity arrays with depth of 1 µm and diameter of 500 nm. We deposited thin layers of TiO_2 and Au to form the Schottky junction. Finite-difference time-domain simulation results in Figure 2a show that thinner Au layers can promote broadband light absorption, which might be beneficial for hot electron generation. Experimental results of the photoresponse in Figure 2b show a peak at around 590 nm, which is below the TiO_2 bandgap. We also tried to achieve multi-band photoresponse by depositing gold nanorods on MSPhC. In order to understand the generation and injection of hot electrons through plasmon decay, we are currently working on modeling and measuring momentum distribution of plasmon-induced hot electrons in metal nanostructures such as gold nanorods.



▲Figure 1: (a) Schematic of 2D micro-cavity arrays of MSPhC. (b) Top view photo of MSPhC via SEM. Scale bars are 1 µm.



▲Figure 2: (a) Simulated absorption spectra of MSPhC for various Au thickness. (b) Photoresponse of MSPhC centered at 590 nm.

FURTHER READING

- J. B. Chou, D. P. Fenning, Y. Wang, M. A. M. Polanco, J. Hwang, F. Sammoura, J. Viegas, M. Rasras, A. Kolpak, S. H. Yang, and S.-G. Kim, “Broadband Photoelectric Hot Carrier Collection with Wafer-Scale Metallic-Semiconductor Photonic Crystals,” *42nd IEEE PVSC*, New Orleans, LA, 2015.
- Y. Wang, J. B. Chou, and S.-G. Kim, “Simulation Study of Metallic Photonic Crystal for Enhanced Hot Electron Transfer in Electrochemical Cells,” presented at *MRS Fall Meeting*, Boston, MA, 2015.
- A. Elfaer, Y. Wang, X. H. Li, J. B. Chou, and S.-G. Kim, “Gold Nanorods Coated Metallic Photonic Crystal for Enhanced Hot Electron Transfer in Electrochemical Cells,” *MRS Advances*, FirstView, pp. 1-7, 2015.

Optimizing Stability and Capacity for Lithium-Air Batteries

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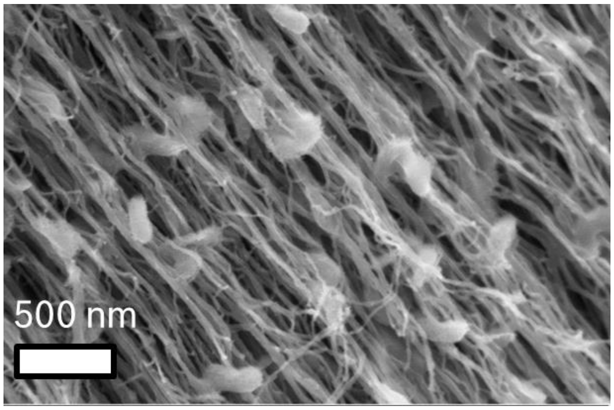
Sponsorship: Skoltech Center for Electrochemical Energy Storage

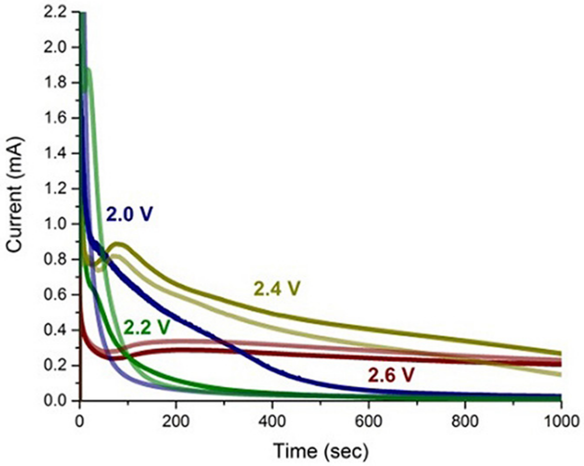
Lithium-air batteries hold promise for the next generation of electric vehicles and other applications. By reacting oxygen directly with lithium ions to form Li_2O_2 on discharge, they can achieve energy densities 3-5 times higher than current lithium-ion batteries. However, a number of challenges exist for implementing lithium-air batteries, including poor rate capability, poor cyclability, high overpotentials upon charging, and electrode and electrolyte instability. We seek to address these issues by developing new electrode materials and architectures and performing studies of Li_2O_2 formation under various discharge conditions.

Aligned arrays of carbon nanotubes (CNTs) provide ideal conductive scaffolding materials for Li_2O_2, while having high void space and low mass. CNTs of 5-10 nm in diameter are grown in aligned forests on catalyst deposited silicon wafers. These forests can be delaminated and placed directly into our cell. We observed near ideal gravimetric capacities and high volumetric capacities. However, carbon has been found to decompose in lithium-air cells and promote electrolyte decomposition. This leads to poor cycling performance and high overpotentials on charge. To avoid these effects, we coated materials such as TiN onto CNTs using atomic layer deposition to chemically passivate the carbon surface. These coated CNTs are capable of supporting Li_2O_2 growth (Figure 1). We are currently working on optimizing conductivity of the deposited films and testing electrochemical performance during charge and cycling.

Another challenge in designing Li-O_2 is obtaining optimal volumetric discharge capacity, which can be achieved by promoting the growth of large toroidal deposits of Li_2O_2 as opposed to thin films, which electrically passivate and cut off cell discharge prior to full void space filling of the electrode. We seek to study the mechanisms of nucleation and growth in order to control these processes. For this study we used carbon paper electrodes for greater reproducibility and facility in modeling. We test these electrodes with potentiostatic discharges, which use a fixed driving force. We can then adapt existing models for electrodeposition to our system to extract rates of surface nucleation and growth based on current transients (Figure 2). By further studying the dependence of these rates on solvent type, potential, and electrode surface, we can find optimal conditions for greater cell capacity and better understand mechanisms of Li_2O_2 evolution.



▲Figure 1: SEM micrograph of toroidal Li_2O_2 formation on CNTs deposited with a coating of TiN.



▲Figure 2: Current transients from potentiostatic discharges at a range of potentials in 0.1 M $LiClO_4$ DMSO. Peaks occur at longer times at higher potentials (lower overpotentials), suggesting slower nucleation/growth rates.

FURTHER READING

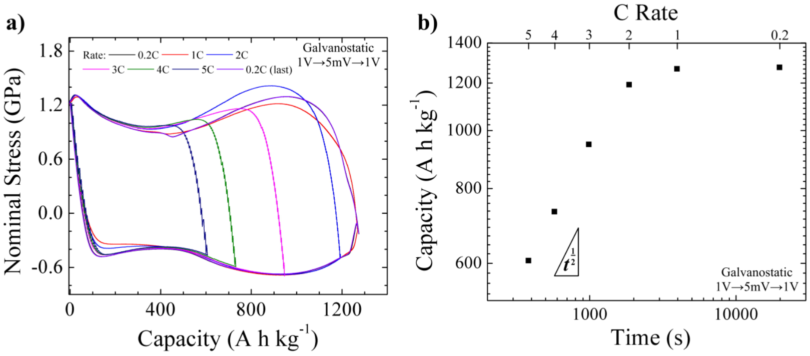
- R. R. Mitchel, B. M. Gallant, Y. Shao-Horn, and C. V. Thompson, "Mechanisms of Morphological Evolution of Li_2O_2 Particles during Electrochemical Growth," *Journal of Physical Chemistry Letters*, vol. 4, no. 7, pp. 1060, March 2013.
- B. M. Gallant, R. R. Mitchell, D. G. Kwabi, J. Zhou, L. Zuin, C. V. Thompson, and Y. Shao-Horn, "Chemical and Morphological Changes of Li–O2 Battery Electrodes upon Cycling," *The Journal of Physical Chemistry C*, vol. 116, no. 39, pp. 20800–20805, October 2012.

Mechanical Stresses in Lithium Phosphorus Oxynitride-Coated Germanium Thin-Film Electrodes

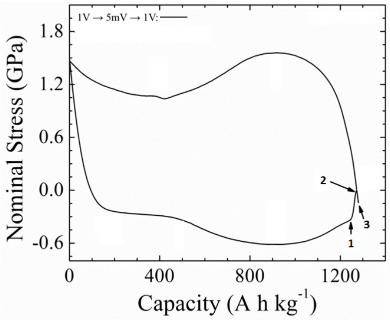
A. Al-Obeidi, D. Kramer, R. Moenig, C. V. Thompson
Sponsorship: SMART

In the electronics and health industry, there has been a strong trend toward miniaturized devices for use in wearable electronics, medical implants, and wireless communication. The reduced energy consumption of microsystems makes it possible to integrate microbatteries directly onto electronic chips. Solid-state microbatteries are ideally suited for such applications since they can be integrated on microchips while offering improved safety (no liquid electrolytes and thermal runaway), performance (higher voltages, wider range of operating temperatures), and lifetime. The simplest and most common form of a solid-state battery is a planar solid-state thin-film battery. For the anode, germanium is an ideal candidate since it offers large volumetric capacities (7366 A h l^{-1}) compared to lithium (2065 A h l^{-1}) while being compatible with conventional semiconductor processing techniques. However, use of germanium is limited by the significant volumetric and structural changes that occur during cycling. In order to explore the relationship between electrochemistry and the mechanical stresses, in situ stress measurements on germanium thin-film electrodes coated with lithium phosphorus oxynitride (LiPON) were performed.

It was found that LiPON, a rigid solid electrolyte, suppresses morphological evolution and results in reproducible cycle-to-cycle stress behavior. The repeatable behavior observed in LiPON-coated films allows more direct characterization of electrochemical processes governing lithiation and delithiation. Cycling at various rates (Figure 1) revealed that the lithiation capacity of coated electrodes increased at slower cycling rates, saturating at about 1200 A h kg^{-1} when using rates slower than 1 C. Cycling below 100 mV resulted in the formation of c-$Li_{15}Ge_4$, which appeared as a sharp drop in the compressive nominal stress to values close to zero (Figure 2, points 1-2). Overlithiation of this phase resulted in a linear compressive increase in stress (Figure 2, points 2-3). These results indicate that c$Li_{15}Ge_4$ has a higher density than its a-Li_xGe precursor. Delithiation of c-$Li_{15}Ge_4$ seems to consist of two successive events: the formation of an intermediate phase followed by a rapid release of lithium from this intermediate phase, which resulted in the amorphization of the electrode. While crystalline $Li_{15}Ge_4$ develops a lower maximum nominal tensile stress than its amorphous counterpart, extraction of lithium from c$Li_{15}Ge_4$ requires more energy and therefore reduces the energy efficiency of a cell.



▲Figure 1: Nominal stress vs. capacity plots for a LiPON-coated 170-nm germanium film cycled galvanostatically (1 V → 5mV → 1 V) at different C rates. The data for the final scan at 0.2 C (purple) overlaps with that of the initial 0.2 C scan (black). The 1 C rate corresponds to 115 μA cm^{-2}.



▲Figure 2: Nominal stress-capacity plots for conditions that lead to the formation of crystalline $Li_{15}Ge_4$ of a LiPON-coated 170-nm-thick germanium electrode cycled galvanostatically at 13.3` μA (i.e., 0.2 C, 23 μA cm^{-2}).

FURTHER READING

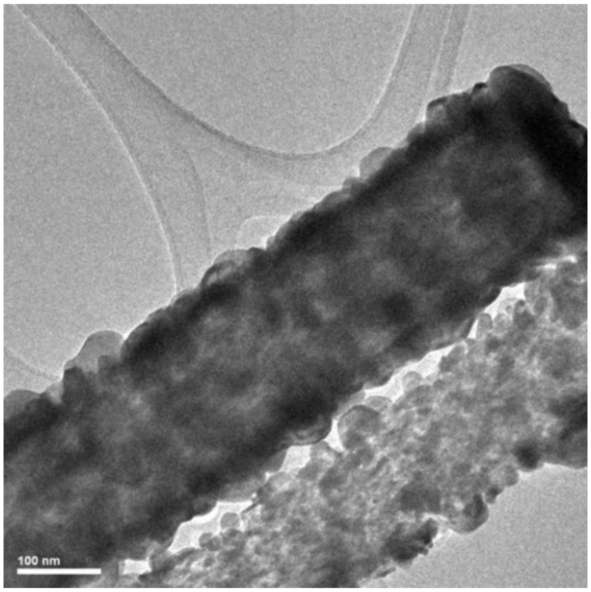
- Z. Choi, D. Kramer, and R. Mönig, "Correlation of Stress and Structural Evolution in Li4Ti5O12-based Electrodes for Lithium Ion Batteries," *Journal of Power Sources*, vol. 240, pp. 245, 2013.
- A. Al-Obeidi, D. Kramer, R. Mönig, and C. V. Thompson, "Mechanical Stresses and Crystallization of Lithium Phosphorous Oxynitride-coated Germanium Electrodes During Lithiation and Delithiation," *Journal of Power Sources*, vol. 306, pp. 817, 2016.

Fabrication of Ruthenium Oxide-Coated Si Nanowire-Based Supercapacitors

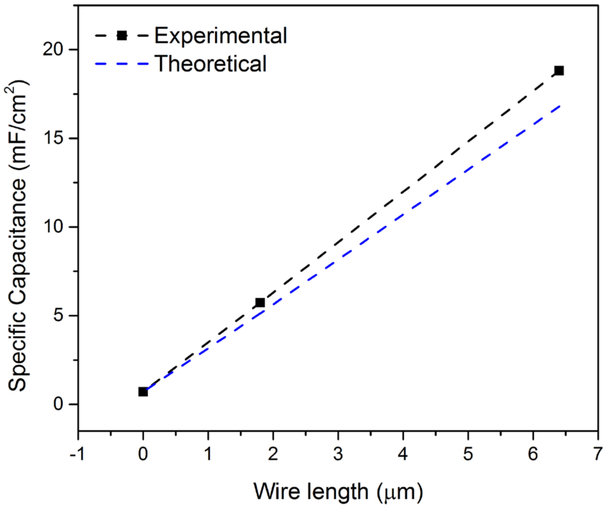
W. Zheng, Q. Chen, D. Wang, C. V. Thompson
Sponsorship: SMART

Supercapacitors are electrochemical devices that have high power density and long cycle life. Pseudo-capacitors are a type of supercapacitor that involves reversible surface reduction/oxidiation reactions. Among all the pseudo-capacitive materials, ruthenium oxide is the most promising due to its high specific capacitance, excellent cyclability, and high conductivity. While researchers have been developing supercapacitors based on ruthenium oxide or its composite with other materials such as carbon nanotubes (CNTs), there has been little study on ruthenium oxide-Si composite electrodes. In earlier work, we demonstrated the feasibility of using metal assisted chemical etching (MACE) to fabricate Si nanowires for on-chip MOS capacitors. Here we use an ordered vertical array of Si nanowires from a similar wet etching process named metal-assisted anodic etching (MAAE) to fabricate on-chip supercapacitors.

Atomic layer deposition (ALD) is used to deposit ruthenium oxide on silicon nanowires due to its conformal coating of high aspect ratio structures. The use of ALD also provides precise control of the ruthenium oxide film thickness. As pseudo-capacitive reactions occur at the surface of ruthenium oxide, the high aspect ratio Si nanowire structures coated with ruthenium oxide has a high surface area of accessible ruthenium oxide per area of substrate surface, which thus leads to a high energy storage capacitance. We have developed an ALD process for coating of ruthenium oxide on Si nanowires generated by MAAE. The composite structure showed a con-tinuous coating of well-distributed particles (Figure 1). High-resolution transmission electron microscopy characterization and x-ray diffraction analysis confirmed that most nanoparticles were in the form of elemental ruthenium. We are currently investigating the electrochemical performance of this composite material in an aqueous electrolyte using a three-electrode setup. The preliminary data showed that the specific capacitance scaled well with the length of silicon nanowires in this aqueous electrolyte (Figure 2). Meanwhile, we are fabricating solid-state micro-supercapacitors based on use of solid electrolytes. We are interested in studying the performance dependence of the solid-state device on both Si nanowire aspect ratios and ALD cycle numbers.



▲Figure 1: TEM image of Si nanowires after ALD coating of ruthenium oxide.



▲Figure 2: Specific capacitance as function of Si nanowire lengths. The black line shows linear fit to experimental data; the blue line shows theoretical projection of the specific capacitance with nanowire lengths.

FURTHER READING

- S. W. Chang, J. Oh, S. T. Boles, and C. V. Thompson, "Fabrication of Silicon Nanopillar-based Nanocapacitor Arrays," *Appl. Phys. Letters,* vol. 96, pp. 153108, 2010.
- S. W. Chang, V. P. Chuang, S. T. Boles, C. A. Ross, and C. V. Thompson, "Densely-packed Arrays of Ultrahigh-aspect-ratio Silicon Nanowire Fabricated Using Block Copolymer Lithography and Metal-assisted Etching," *Adv. Funct. Mater.,* vol. 19, pp. 2495, 2009.
- C. Q. Lai, W. Zheng, W. K. Choi, and C. V. Thompson, "Metal Assisted Anodic Etching of Silicon," *Nanoscale,* vol. 25, pp. 11123, 2015.

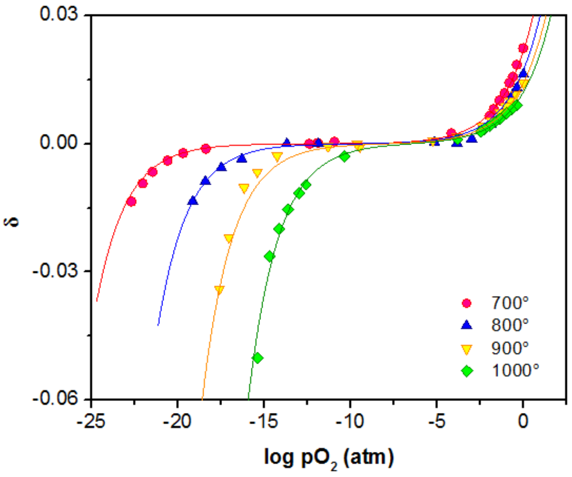
Electro-Chemo-Mechanical Studies of Perovskite-Structured Mixed Ionic-Electronic Conducting $SrSn_{1-x}Fe_xO_{3-x/2+\delta}$

C. S. Kim, S. R. Bishop, N. H. Perry, H. L. Tuller

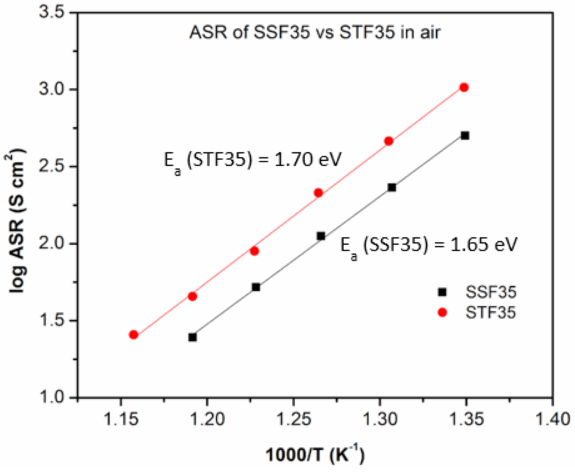
Sponsorship: Skolkovo Foundation

High efficiency and fuel flexibility make solid oxide fuel cells (SOFCs) attractive for conversion of fuels to electricity. Reduced operating temperatures, desirable for reduced costs and extended operation, however, result in significant losses in efficiency. This loss has been traced primarily to slow cathode surface reaction kinetics. In this work, we extend previous studies on the promising mixed ionic and electronic conducting perovskite-structured $SrTi_{1-x}Fe_xO_{3-x/2+\delta}$ (STF) materials system whose exchange kinetics were correlated with the minority electron charge density by replacing Ti with Sn, due to its distinct band structure and higher electron mobility.

Oxygen nonstoichiometry and the defect chemistry of the $SrSn_{1-x}Fe_xO_{3-x/2+\delta}$ (SSF) system were examined by thermogravimetry as a function of oxygen partial pressure in the temperature range of 973-1273 K. Marginally higher reducibility was observed compared to corresponding compositions in the STF system. The bulk electrical conductivity was measured in parallel to examine how changes in defect chemistry and electronic band structure, associated with the substitution of Ti by Sn, impact carrier density and ultimately electrode performance. Bulk chemical expansion was measured by dilatometry as a function of oxygen partial pressure, while surface kinetics were examined by means of AC impedance spectroscopy. The electro-chemo-mechanical properties of SSF were found not to differ significantly from the corresponding composition in STF. Key thermodynamic and kinetic parameters for $SrSn_{0.65}Fe_{0.35}O_{2.825+\delta}$ (SSF35) were derived, including the reduction enthalpy, electronic band gap, anion Frenkel enthalpy, oxygen vacancy migration energy, and electron and hole mobilities. Though slightly shifted by the larger size of Sn, the defect equilibria and the cathode area specific resistance differed only in a limited way from that in STF. This was attributed to properties being largely dominated by Fe and not by the substitution of Ti with Sn.



▲Figure 1: Oxygen nonstoichiometry δ as a function of pO_2 and temperature for SSF35.



▲Figure 2: Comparison of temperature dependence of area specific resistance (ASR) of SSF35 and STF35 thin film electrodes.

FURTHER READING

- W. Jung and H. L. Tuller, "A New Model Describing Solid Oxide Fuel Cell Cathode Kinetics: Model Thin Film $SrTi_{1-x}Fe_xO_{3-\delta}$ Mixed Conducting Oxides, a Case Study," *Advanced Energy Materials*, vol. 1, pp. 1184–1191, 2011.

Utilization of $BaSnO_3$ and Related Materials Systems for Transparent Conducting Electrodes

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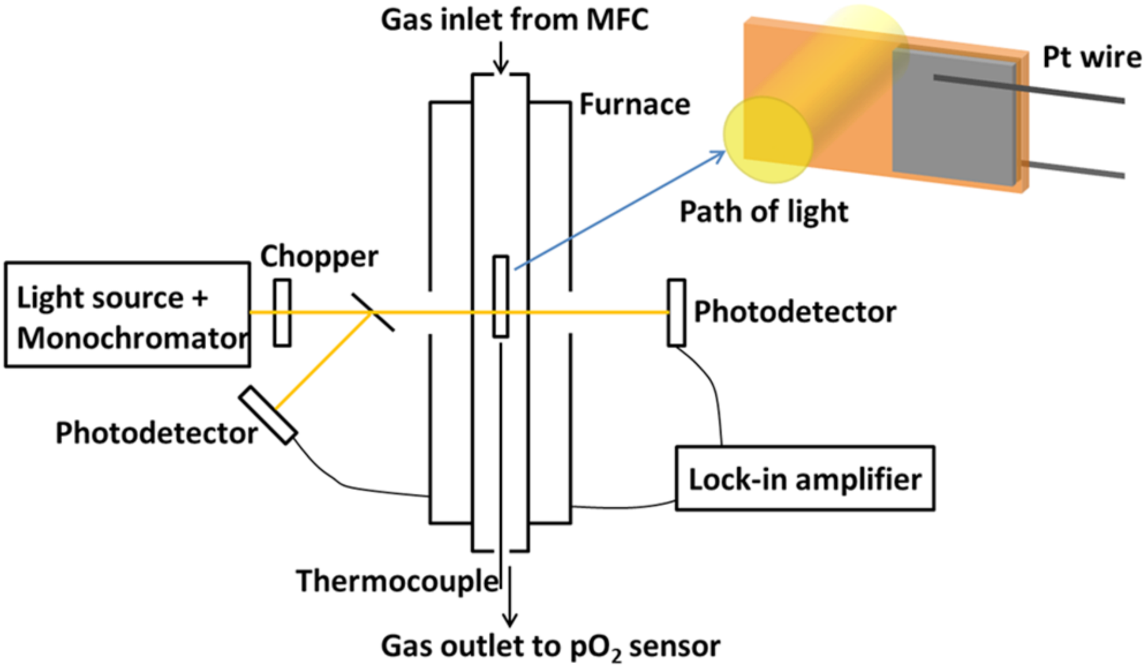
Sponsorship: NSF

Efficient transparent electrode materials are vital for applications in smart window, LED display, and solar cell technologies. These materials must possess a wide band gap for minimal optical absorption in the visible spectrum while maintaining a high electrical conductivity. Tin-doped indium oxide (ITO) has been the industry standard for transparent electrodes, but the use of the rare element indium has led to a search for better material alternatives. $BaSnO_3$ represents a promising alternative due to its high electron mobility and resistance to property degradation under oxidizing conditions, but the mechanisms by which processing conditions and defect chemistry affect the final material properties are not well understood.

This work seeks to better understand the relationships between processing, defect chemistry, and material properties of $BaSnO_3$ in order to better establish the consistent and controllable use of $BaSnO_3$ as a transparent electrode. To accomplish these goals, methods such as *in-situ* resistance and impedance monitoring during annealing will be applied. In addition, a variety of novel methods such as the *in-situ* monitoring of optical transmission (shown in Figure 1) during annealing and the *in-situ* monitoring of resistance during physical vapor deposition will be utilized to investigate $BaSnO_3$. Direct measurements of the key constants for the thermodynamics and kinetics of oxidation in donor-doped $BaSnO_3$ will be experimentally determined for the first time. This increase in understanding will provide a predictive model for determining the optical properties, carrier concentrations, and electron mobilities in $BaSnO_3$.



▲ Figure 1: Schematic of experimental setup to be used for simultaneous in-situ measurement of the optical transmission and electrical conductivity of thin film $BaSnO_3$ samples during annealing under controlled atmosphere and temperature.

FURTHER READING

- D. O. Scanlon, "Defect Engineering of BaSnO3 for High-performance Transparent Conducting Oxide Applications," *Phys. Rev.* vol. 87, no. 16, pp. 161201, April 2013.
- J. J. Kim, S. R. Bishop, N. J. Thompson, D. Chen, and H. L. Tuller, "Investigation of Nonstoichiometry in Oxide Thin Films by Simultaneous *in Situ* Optical Absorption and Chemical Capacitance Measurements: Pr-Doped Ceria, a Case Study," *Chemistry of Materials*, vol. 26, pp. 1374-1379, 2014.

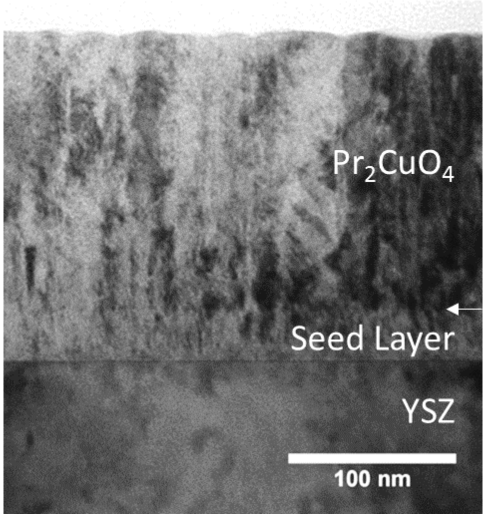
Oxygen Reduction Kinetics and Defect Chemistry of Layered Praseodymium Cuprate-Based Materials

C. S. Kim, K. Mukherjee, S. R. Bishop, H. L. Tuller in collaboration with Y. Hayamizu, S. Istomin

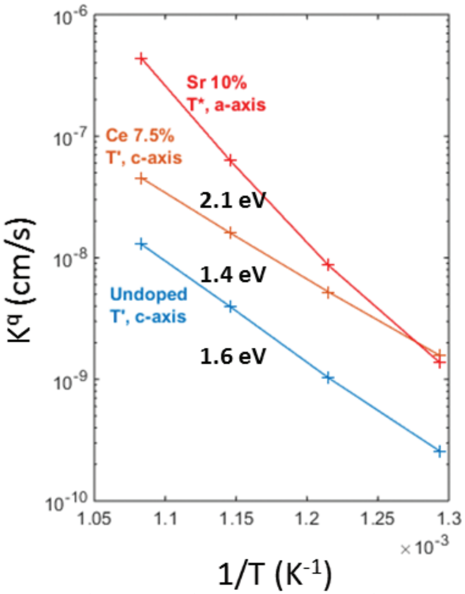
Sponsorship: Skolkovo Foundation

Layered cuprate compounds with mixed ionic electronic conductivity are promising candidate materials for cathodes in intermediate-temperature solid oxide fuel cells. There have been reports of anisotropic oxygen diffusion in materials with the K_2NiF_4 (T) and Nd_2CuO_4 (T') crystal structures, with facile transport along the rock-salt layers. These material systems also exhibit anisotropic thermal and chemical expansion properties, potentially important for long-term device stability. However, in practice, it is difficult to independently control the crystal structure, doping, and grain orientation to understand their effects on cathode performance. Additionally, the lanthanide cuprates exhibit a third phase (T*), a hybrid of the T and T' phases, with important implications for the ionic and electronic conductivity.

In this work, we aim to understand the correlation between defect chemistry and surface exchange kinetics. Oxygen nonstoichiometry of Pr_2CuO_4 with varying amounts of Sr and Ce doping is studied as a function of oxygen partial pressure and temperature by thermogravimetry. Fitting the nonstoichiometry data to defect models enables the derivation of thermodynamic parameters as well as defect carrier concentrations. Dopants added to praseodymium cuprate were found to considerably extend the range of oxygen nonstoichiometry. Thins films of corresponding compounds were prepared by pulsed-laser deposition onto single-crystal YSZ substrates. Alloys with the same crystal structure and doping but with different film orientations were also successfully synthesized through the use of seed layers on YSZ (Figure 1). Using electrochemical impedance spectroscopy to measure the area-specific resistance (ASR), we found a significant improvement in the oxygen surface-exchange rate as a result of both donor and acceptor doping (Figure 2). However, the activation energies are very different, indicative of different rate-determining steps in each case. Also, contrary to expectations, the effect of film orientation (fast oxygen diffusion axis vs. slow diffusion axis) had only a relatively weak effect on the ASR. The reason for this weak correlation between the film orientation and the ASR is under investigation.



▲ Figure 1: Cross-sectional TEM of a Pr_2CuO_4 thin film grown epitaxially on a YSZ substrate. The columnar grains are a result of tetragonal film on cubic substrate resulting in two possible in-plane orientations.



▲ Figure 2: Oxygen surface exchange as a function of inverse temperature in Pr_2CuO_4 thin films as determined from the area-specific resistance by electrochemical impedance spectroscopy. The activation energies are listed.

FURTHER READING

- M. Burriel, G. Garcia, J. Santiso, J. A. Kilner, R. J. Chater, and S. J. Skinner, "Anisotropic Oxygen Diffusion Properties in Epitaxial Thin Films of $La_2NiO4+\delta$," *Journal of Materials Chemistry*, vol. 18, pp. 416-422, 2008.
- G. N. Mazo, Y. A. Mamaev, M. Z. Galin, M. S. Kaluzhskikh, and A. K. Ivanov-Schitz, "Structural and Transport Properties of the Layered Cuprate Pr_2CuO_4," *Inorganic Materials*, vol. 47, pp. 1218–1226, 2011.
- H. Y. Hwang, S.-W. Cheong, A. S. Cooper, L. W. Rupp Jr., B. Batlogg, and G. H. Kwei, "Crystallographic Evolution, T'→T*→T, in $Pr_{2-x}Sr_xCuO_{4-\delta}$," *Physica C: Superconductivity*, vol. 192, pp. 362–371, 1992.

Investigation of Fuel Cell Cathode Performance in Solid Oxide Fuel Cells: Application of Model Thin Film Structures

J. J. Kim, D. Chen, N. H. Perry, S. R. Bishop, H. L. Tuller

Sponsorship: DOE

An improved fundamental understanding of oxygen nonstoichiometry (δ) and surface exchange kinetics in solid oxide fuel cell (SOFC) cathodes is considered critical for achieving enhanced device performance and longevity, especially at reduced operating temperatures. Although numerous research activities have been focused on elucidating the oxygen reduction reaction (ORR) mechanisms at the cathode, their conclusions remain unsatisfactory and controversial. The ORR at mixed conducting oxide thin film cathodes consists of oxygen adsorption, dissociation, charge-transfer, incorporation, and migration of charge carriers. The kinetic parameters associated with the overall ORR, such as the diffusion coefficient (D) and surface exchange coefficient (k), are strongly influenced by δ in the oxides. On the other hand, oxygen defect generation is often associated with valence changes in the transition metal or rare earth ions within the oxides and corresponding changes in lattice constant (chemical expansion). This phenomenon may lead to stresses sufficient to support crack initiation and/or delamination, impacting the device's long-term stability. Because many advanced oxide materials used in SOFCs experience significant changes in δ during operation at elevated temperatures and under reducing/oxidizing conditions, the ability to diagnose a material's behavior *in situ* is, therefore, important.

Our group recently demonstrated that δ in $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ (10 PCO) thin films could be reliably derived by utilizing chemical capacitance extracted from electrochemical impedance spectroscopy (EIS) measurements. Furthermore, we introduced a non-contact optical means for *in situ* recording of transient redox kinetics, as well as the equilibrium Pr oxidation state and, in turn, δ in 10 PCO thin films, by monitoring the change in absorption spectra upon change in pO_2 or temperature. Recently, these optical techniques have been extended by our group to examination of the perovskite SOFC electrode $Sr(Ti,Fe)O_{3-\delta}$. In this study, we are investigating cathode kinetics and nonstoichiometry of two model oxide thin films, $Sr(Ti,Fe)O_{3-\delta}$ (STF) with La doping and $(Pr,Ce)O_{2-\delta}$ (PCO), by simultaneously utilizing *in situ* and *in operando* optical absorption spectroscopy and EIS as a function of temperature, pO_2 and electrical potential. We are also investigating changes in surface chemistry and their impact on electrode impedance by atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), and low-energy ion scattering spectroscopy (LEIS).

FURTHER READING

- D. Chen, S. R. Bishop, and H. L. Tuller, "Non-stoichiometry in Oxide Thin Films Operating Under Anodic Conditions: A Chemical Capacitance Study of the Praseodymium-cerium Oxide System," *Chemistry of Materials*, vol. 26, no. 22, pp. 6622-6627, 2014.
- N. H. Perry, D. Pergolesi, S. R. Bishop, and H. L. Tuller, "Defect Chemistry and Surface Oxygen Exchange Kinetics of La-doped $Sr(Ti,Fe)O_{3-a}$ in Oxygen-rich Atmospheres," *Solid State Ionics*, vol. 273, pp. 18-24, 2015.
- J. J. Kim, S. R. Bishop, N. J. Thompson, D. Chen, and H. L. Tuller, "Investigation of Nonstoichiometry in Oxide Thin Films by Simultaneous in Situ Optical Absorption and Chemical Capacitance Measurements: Pr-doped ceria, a Case Study," *Chem. Mater.*, vol. 26, pp. 1374-1379, January 2014.

Coupling of Oxide Catalyst Chemistry with Durability and Conversion Efficiency for Biomass Reforming

V. Mortola, S. R. Bishop, H. L. Tuller in collaboration with M. Shetty, Y. Roman
Sponsorship: Basic Energy Sciences/DOE

The transportation sector currently relies heavily on non-renewable fossil-based fuels to meet its energy requirements. Alternative energy sources need to be developed to meet the projected energy demand in the future in a sustainable and environmentally conscious manner. Bio-oils, generated via biomass fast pyrolysis, represent an attractive avenue for the production of renewable fuels and chemicals. We are investigating $MoO_{3-\delta}$, a promising catalyst for bio-oil upgrading, that selectively transforms various phenolic compounds into aromatic hydrocarbons with high yields using low H_2 pressures by hydrodeoxygenation (HDO). While it is clear that both ionic (oxygen vacancies) and electronic defects (e.g., $Mo^{5+/3+}$), in both the oxide catalyst and oxide support (e.g., TiO_2, ZrO_2 and Al_2O_3), play controlling roles in the catalytic reactions, surprisingly little is known about how operating conditions (temperature, dopants/impurities, and atmosphere (pO_2, pH_2O, pH_2, carbon activity, etc.)) impact the concentration or the diffusivities of these key defects, or how they influence the reaction kinetics. In this project, we combine catalysis with defect chemical and impedance spectroscopic approaches to achieve a deeper understanding of the role that defects in metal oxide catalysts and supports play in influencing catalytic selectivity, efficiency, stability, and reaction rates.

FURTHER READING

- T. Prasomsri, M. Shetty, K. Murugappan, and Y. Roman-Leshkov, "Insights into the Catalytic Activity and Surface Modification of MoO_3 During the Hydrodeoxygenation of Lignin-derived Model Compounds into Aromatic Hydrocarbons Under Low Hydrogen Pressures," *Energy Environ. Sci.*, vol. 7, pp. 2660, 2014.
- T. Prasomsri, T. Nimmanwudipong, and Y. Roman-Leshkov, "Effective Hydrodeoxygenation of Biomass-derived Oxygenates into Unsaturated Hydrocarbons by MoO_3 Using Low H_2 Pressures," *Energy Environ. Sci.*, vol. 6, pp. 1732, 2013.

Synthesis of CRUD and its Effects on Pool and Subcooled Flow Boiling

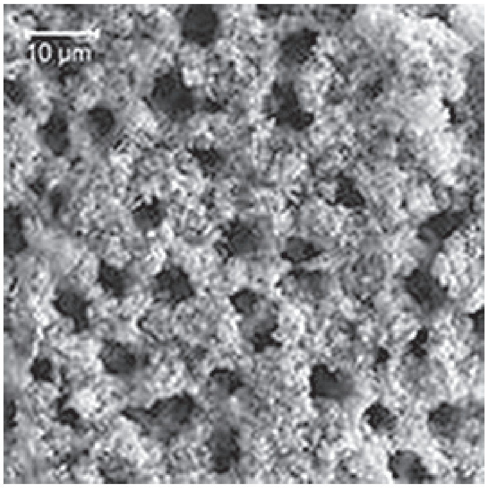
C. P. Coyle, B. A. Phillips, S. P. Lowder, J. Buongiorno, M. Bucci, T. McKrell

Sponsorship: DOE, Office of Nuclear Energy

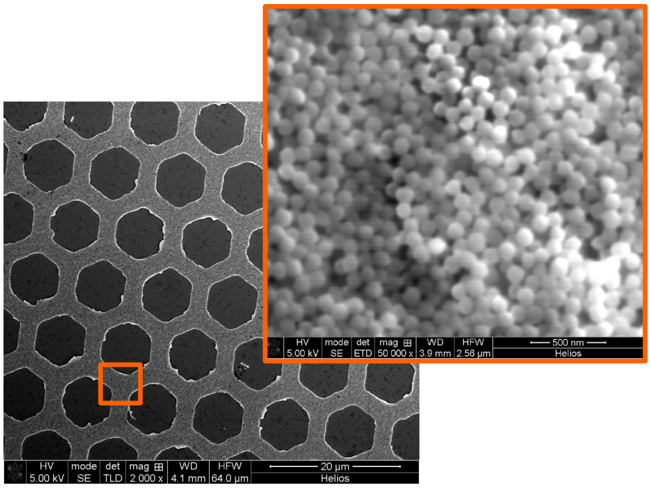
Chalk River Unidentified Deposits (CRUD) are a naturally occurring porous, hydrophilic layer that forms on fuel rods during nuclear reactor operation. Unique features of these deposits are the characteristic boiling chimneys, as shown in Figure 1. It has been hypothesized that the presence of these chimneys, by providing a clear path for vapor escape, can further enhance boiling properties such as critical heat flux and heat transfer coefficient.

An investigation of such effects has been conducted by preparing a porous, hydrophilic layer with boiling chimneys on indium-tin-oxide-coated sapphire heaters. A porous matrix emulating CRUD, shown in Figure 2, was created using layer-by-layer deposition of 100-nm silica nanoparticles to form porous, hydrophilic thick films. Photolithography was used to manufacture posts that were then dissolved to create characteristic boiling chimneys. MTL facilities were used to deposit gold pads on the heater, plasma clean heaters, create and remove photoresist posts, and confirm film thickness using the Dektak profilometer. Features such as thickness, wettability, pore size, and chimney diameter and pitch were verified. During pool and flow boiling testing, IR thermography and high-speed video were used to obtain temperature profiles of the active heater area to quantify properties such as heat transfer coefficient, nucleation site density, bubble departure frequency, and bubble departure diameter.

Data from pool and subcooled flow boiling tests has shown that the heat transfer coefficient increases with increasing layer thickness and chimney diameter while the chimney pitch has relatively no effect. The observed increase results from greater nucleation site densities and greater bubble departure frequencies, meaning the surface is able to remove more heat through the creation of more bubbles per unit area and per unit time. The bubble parameters also followed expected trends with mass flux and imposed heat flux.



▲ Figure 1: SEM image of actual reactor CRUD (note the micro-scale boiling chimneys).



▲ Figure 2: SEM image of synthetic CRUD with a zoom-in of the nanoporous CRUD matrix in between the boiling chimneys.