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Ceria based inverse opals for thermochemical fuel production: Quantification and prediction of high temperature behavior

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Materials Science and Engineering

by

Danielle Courtney Casillas

2015

ABSTRACT OF THE DISSERTATION

Ceria based inverse opals for thermochemical fuel production: Quantification and prediction of high temperature behavior

by

Danielle Courtney Casillas Doctor of Philosophy in Materials Science and Engineering University of California, Los Angeles, 2015 Professor Bruce S. Dunn, Chair

Solar energy has the potential to supply more than enough energy to meet humanity's energy demands. Here, a method for thermochemical solar energy storage through fuel production is presented. A porous non-stoichiometric oxide, ceria, undergoes partial thermal reduction and oxidation with concentrated solar energy as a heat source, and water as an oxidant. The resulting yields for hydrogen fuel and oxygen are produced in two discrete steps, while the starting material maintains its original phase.

Ordered porosity has been shown superior to random porosity for thermochemical fuel production applications, but stability limits for these structures are currently undefined. Ceriabased inverse opals are currently being investigated to assess the architectural influence on thermochemical hydrogen production. Low tortuosity and continuous interconnected pore network allow for facile gas transport and improved reaction kinetics. Ceria-based ordered materials have recently been shown to increase maximum hydrogen production over non-ordered porous ceria.

Thermal stability of ordered porosity was quantified using quantitative image analysis. Fourier analysis was applied to SEM images of the material. The algorithm results in an order parameter gamma that describes the degree of long range order maintained by these structures, where $\gamma > 4$ signifies ordered porosity. According to this metric, a minimum zirconium content of 20 atomic percent (at%) is necessary for these architectures to survive aggressive annealing up to 1000°C. Zirconium substituted ceria (ZSC) with Zr loadings in excess of 20at% developed undesired tetragonal phases. Through gamma, we were able to find a balance between the benefit of zirconium additions on structural stability and its negative impact on phase. This work demonstrates the stability of seemingly delicate architectures, and the operational limit for ceria based inverse opals to be 1000°C for 1µm pore size. Inverse opals having sub-micron pores did not sustain ordered structures after heating, and those larger than 1µm had reinforced structural stability. Furthermore, this analysis was applied to materials which underwent isothermal hydrogen/water redox cycles. ZDC20 inverse opals having 300, 650 and 1000nm pore sizes maintained ordered porosity at 800°C, indicating a novel opportunity for use at higher temperatures.

The mechanism of inverse opal degradation was investigated. Both *in situ* and *ex situ* electron microscopy studies were performed on inverse opals subjected to high temperatures. Coarsening by surface diffusion was found to be the dominant grain growth mechanism. The inverse opal grain growth mechanism was found to deviate from that of porous materials due to the high porosity and an upper limit to grain size caused by structural confinement. Furthermore, *in situ* experiments

enabled correlation of nano-scale grain growth to micro-scale feature changes, resulting in an empirical relationship.

Lastly, this dissertation presents an investigation of the effect of ordered porosity on hydrogen production rate and quantity. These results differ from those presented in literature, and an opportunity for further investigation is proposed. The dissertation of Danielle Courtney Casillas is approved.

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2015

To My Parents, Sister, and Brother

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Chapter 1: Introduction to Thermochemical Hydrogen Production

Chapter 1.1 Motivation

Tapping our most abundant resource, solar radiation, remains a scientific and engineering challenge. The daily amount of sunlight striking the Earth's surface potentially provides vastly more energy than humans need to survive. However, sunlight is diffuse and intermittent, and efficient capture varies greatly by geographical location. Hence, utilization of solar energy requires both direct conversion and storage¹.

Among the methods of solar energy storage, thermochemical fuel production has the most potential, in terms of energy density and cost. Thermochemical processes, especially those relying on concentrated solar energy, have potentially high conversion efficiencies². Current progress in thermochemical fuel production focuses on both the development of novel systems, and also enhancement of well-established catalyst materials, including those used for two-step thermochemical cycles.

Efforts to improve kinetics of fuel production include manipulation of morphology and macroscopic architecture. During the past two decades, materials with ordered porosity have emerged in applications beyond photonic crystals³. Specifically, the thermochemical cycling capability of cerium oxide is improved by templating ordered porosity, and by dopant additions⁴. Accessible surface area, though not total surface area, is increased in materials with ordered porosity by decreasing reactant gas path tortuosity and increasing pore connectivity. Maintaining these structures at the temperatures required for thermochemical fuel production (>1000°C) is a challenge, as ceria coarsens extensively at these temperatures.

Another feature of ceria is that small additions of zirconium improve overall kinetics of oxygen up-take and release, overall fuel production efficiency, and inhibit grain growth and coarsening^{5,6,7}.

In these materials, oxygen defects, specifically vacancies, play a larger role than surface area in the catalytic efficiency⁸. Non-stoichiometric oxides such as ceria can have high oxygen storage capacity and anion mobility in the cubic phase, especially distorted pseudocubic (t'') phase, due to large oxygen vacancy concentration^{9,10}.

The current limitation of nonstoichiometric metal oxides for thermochemical fuel production is their low oxygen storage capacity when compared to stoichiometric systems¹¹. Oxygen storage capacity arising from nonstoichiometry, δ , is directly related to solar to fuel production efficiency. Thus fully stoichiometric reactions involving complete reduction of metal oxides are inherently more efficient, as more fuel can be produced. Although progress has been made towards the improvement of oxygen storage capacity of nonstoichiometric oxides, specifically ceria, their fuel production capacity is still much less than that of stoichiometric oxides. In order gain a competitive advantage over stoichiometric materials, the benefits of fast kinetics and cyclability must outweigh that of total oxygen storage capacity for a given amount of time.

Chapter 1.2 Objectives

This dissertation addresses three problems associated with the implementation of inverse opal architectures: a) determining the degree of order present in materials after high temperature treatments, b) attempting to understand the underlying mechanism of disorder by coarsening, and c) addressing the difference in hydrogen production ability of inverse opals to bulk materials. The goal of these three is to quantify and predict structural changes to ceria inverse opals under operating conditions in order to assess feasibility of these materials for practical applications. This dissertation introduces a method to quantify order of inverse opals subjected to conditions which mimic cycling conditions. A previously developed method to assess the quality of ordered porosity

of anodic aluminum oxide (AAO) has been adopted. The analysis is based on an order parameter is extracted from the fast Fourier transform data acquired from SEM images of inverse opal materials. In addition, a mechanism to explain coarsening phenomena in oxide inverse opals is introduced, and grain growth data obtained by TEM image measurements is fit to existing models. Lastly, hydrogen production and rate are compared between materials having the same composition but different porosity characteristics.

Chapter 1.3 Thermochemical processes

Thermochemical fuels offer a route to the storage of energy contained in sunlight. While solar cells and similar technologies create electricity for immediate use, solar thermochemical fuels can be stored indefinitely. Storage of solar fuel is crucial to both the supplementation of grid power during peak energy usage hours and for transportation applications, if our society is to move towards total dependency on sustainable energy sources.

Early interest in hydrogen as a thermochemical fuel was prompted by an interest in improving existing hydrogen production methods, including electrolysis of water¹². Continuing interest in hydrogen production stems from the fact that the only products of hydrogen combustion are energy and water, and water-splitting can produce hydrogen. The most straightforward method of hydrogen production from water is through thermolysis, where there is no PV work in the form of Gibbs free energy¹³ added to the system:

$$\Delta G = \Delta H - T \Delta S \quad (1)$$

where $\Delta G=0$ for water splitting to occur. However, this reaction takes place ~4700K, which requires a large thermal energy input. Moreover, oxygen and hydrogen are released in the same

step, and complex methods must be used to separate usable hydrogen from oxygen. In order to lower the thermolysis temperature, work in the form of electrical potential can be added to the system. However, the problem of chemical separation of hydrogen and oxygen remains.

Water-splitting can occur in multiple steps without the addition of work¹⁴. Each reaction step has its own entropy, and the summation of all reaction enthalpies can satisfy the following equation for a zero-work requirement¹⁵:

$$\sum S \ge \frac{\Delta G}{(T_H - T_c)} \quad (2)$$

Since this realization, numerous reaction schemes have been proposed for water-splitting.¹⁶

Multiple-step metal oxide redox cycles take advantage of this zero-work input entropy requirement. There are a plethora of reactions to choose from, but only a fraction of known cycles achieve full production of fuel in two individual steps.^{16,17,18} Iron oxide was introduced in 1977 as the first redox pair for two-step solar fuel production¹⁹, according to the following equations:

$$Fe_3O_4 \to 3FeO + \frac{1}{2}O_2$$
 $T_H = 2500K$

$$3FeO + H_2O(g) \to Fe_3O_4 + 2H_2 \quad T_C > 1000K$$

However, the temperatures required for reduction and re-oxidation of Fe_2O_3 and FeO at atmospheric pressure exceed 2500K and 1000K, respectively, which is higher than the melting temperature of both oxides. Although impractical, the Fe_2O_3 cycle served as an introduction to the field of metal oxide redox for thermochemical fuel production.

In the 40 years since their introduction, progress has been made towards the development of new metal oxide systems, motivated by the need for high solar to fuel efficiencies at lower temperatures. The ZnO(s)/Zn(g) cycle is an example of a benchmark in which ZnO is thermally reduced completely to Zn vapor. These volatile systems typically have high oxygen storage capacity due to ease of reduction. However, issues with vapor quenching and the need for nanoparticle morphologies for kinetics considerations have been investigated, but have yet to be resolved^{20,21}. The Zn/ZnO cycle can theoretically produce 12.3 mmol H₂ per gram.^{22,23} The MO₂O₃/MO non-volatile systems such as doped Fe₂O₃/FeO have high oxygen storage capacity and theoretical yield when optimally doped with metallic cations (4.3 mmol H₂/g Fe₃O₄^{24,25}), but the kinetics of these reactions remain slow and particle sintering is a problem for long term cycling.

The generalized form of the two-step metal oxide reduction/oxidation for hydrogen production is:

Reduction at higher temperature
$$(T_H)$$
:
 $\frac{1}{\delta}MO_y \xrightarrow{+\Delta h} \frac{1}{\delta}MO_{y-\delta} + \frac{1}{2}O_2(g)$

Oxidation at lower temperature (T_L) : $H_2O(g) + \frac{1}{\delta} MO_{y-\delta} \xrightarrow{-\Delta h} \frac{1}{\delta} MO_y + H_2(g)$

Total:

$$H_2 O(g) \longrightarrow \frac{1}{2} O_2 + H_2(g)$$

The first step involves the metal oxide reduction at elevated temperatures. Reduction temperatures vary depending on the material, but generally exceed 1273K. In order to reach these temperatures using solar energy, solar concentrators are used. An example of a solar thermochemical reactor powered by concentrated solar energy is shown in Figure 1.



Figure 1: Schematic of solar thermochemical reactor using porous cerium oxide²⁶.

To circumvent the issues of high temperature morphological and structural stability, oxides which favor reduction at moderate temperatures are ideal. Unlike stoichiometric oxide systems that form solid solutions, non-stoichiometric oxides are partially reduced at temperatures lower than those for fully stoichiometric oxides while maintaining original crystal structures.

Chapter 1.4 Cerium Oxide as a Catalyst Material

Cerium oxide was first introduced in 2006 for the application of thermochemical hydrogen production by the CeO₂/Ce₂O₃ stoichiometric redox system, but required substantial temperatures (2000°C) for efficient reaction yields (2.9 mmol H₂ per gram²⁷). Chueh and Haile introduced ceria in its nonstoichiometric form as an alternative to traditional thermochemical redox pairs, requiring lower temperatures (800°C to 1500°C) without undergoing phase changes in the process^{28,132}. Fully oxidized cerium oxide exists in the cubic fluorite phase under ambient temperatures and pressures (Figure 2).



Figure 2: a) Cubic fluorite crystal structure of CeO_2^{28} and b) CeO_2 -ZrO₂ phase diagram based on Raman and XRD measurements²⁹.

Under reducing conditions, a fraction of Ce^{4+} is reduced to Ce^{3+} , and a net charge balance is achieved by the formation of positive oxygen vacancies. The non-stoichiometry δ of $CeO_{2-\delta}$ indicates vacancy concentration. Non-stoichiometric oxides such as ceria can have high oxygen storage capacity and anion mobility in the cubic phase, especially the distorted pseudocubic (t") phase, due to large oxygen vacancy concentration.^{9,10} Remarkably, ceria can maintain its cubic fluorite structure under reducing conditions for a maximum δ of 0.25.²⁷

Chapter 1.4.1 The Role of Zirconia

Pristine cerium oxide, or ceria, has many features which make it attractive for catalyst applications, but with the addition of zirconia, these features are enhanced. Although ceria has a high melting temperature of 2,400°C, rapid grain growth occurs at temperatures above 800°C⁸⁸. Pure ceria in the nanocrystalline form can have enhanced oxygen storage capacity due to the high grain boundary to volume ratio, and high defect concentration at grain boundaries. However, this benefit is lost upon operation at high temperatures, at which ceria is most often used.

Zirconium oxide additions to metal oxides are known to inhibit coarsening. A well-known refractory material, zirconia has a high melting temperature of 2715°C. At room temperature, zirconia exists in the monoclinic phase. In the case of ceria, small zirconium additions improve overall kinetics of oxygen uptake and release, increase overall fuel production efficiency, and inhibits grain growth and coarsening^{5,6,7}. For the established field of TWCs, this translates to improved buffering ability, while for thermochemical fuel production, zirconia additions offer the prospect of lower operating temperatures while maintaining high gravimetric fuel production^{10,30,31}.

Zirconia and ceria have a large solubility range, as indicated by the phase diagram for bulk ceria (Figure 2). Onset of the tetragonal phase can be avoided by maintaining concentrations below ~20 at%. However, above this amount, tetragonal phases can develop which are known to have

low oxygen mobility and storage capacity³². Nano-sized ceria can suppress tetragonal phase formation, but at the temperatures required for thermochemical fuel production, small nanoparticles cannot be sustained at low zirconia concentrations³³.

Current thermodynamic and kinetic analyses indicate an improvement of fuel productivity and production rate with the addition to zirconium to cerium oxide³⁴. Thermodynamic improvements can be attributed to the Zr preference for 7-fold coordination within the cubic lattice. This can be achieved when cerium exists in the Ce³⁺ oxidation state, thus allowing for oxygen vacancies³⁴. Recently, the fuel production of ZSC (zirconium substituted ceria) systems (Ce_{1-x}Zr_xO₂, x=0.25), reached 0.24 mmol/gram³¹. The kinetic advantage of zirconium additions are currently limited to isothermal systems, and improvements in heat recovery are necessary for implementation in two-temperature systems³⁴.

Chapter 1.5 Thermodynamic and kinetic considerations

Chapter 1.5.1 Thermodynamics

Zirconia has long been recognized as an additive to ceria for its ability to improve the ceria's oxygen storage capacity. Until recently, most catalysis literature attributed enhanced oxygen storage capacity (OSC) to greater oxygen mobility in ceria substituted with zirconia.^{35,36,37} However, oxygen storage capacity is a thermodynamic phenomenon, and therefore it is useful to explain it in thermodynamic terms. Nonstoichiometric cerium oxide has inherently high oxygen storage capacity and ion mobility due to a large oxygen vacancy concentration and the openness of the tetrahedral site of the cubic fluorite phase^{29,5,6}. From atomistic simulations, the findings of Balducci et al and Andersson et al confirm that the reduction energy of Ce⁴⁺ is greatly reduced with the addition of Zr^{37,38}. Several authors suggested the difference in ionic radius between cerium and zirconium cause structural defects, increasing the rate of oxygen mobility through the lattice. In addition, the Ce⁴⁺ and Zr⁴⁺ ionic radii difference distorts the cubic lattice, making defects energetically favorable.^{6,39} This hypothesis is supported by Wang *et al*, who used atomistic simulations to show increases in M-O bond energies with increasing Zr content. However, decreases in relaxation energy outweigh bond energy effects. Thus ceria with Zr additions effectively favors oxygen vacancy formation up to a Zr content of 50 at%⁴⁰. Additional atomistic simulations show that oxygen vacancies form most easily next to Zr^{4+} cations, and further, that Zr^{4+} prefer to exist in 7-fold coordination. This 7-fold coordination occurs in ceria, in which cations are normally 8-fold coordinated, when Ce⁴⁺ is reduced to Ce³⁺, and an oxygen vacancy is formed^{41,42}.

Recently, the hypothesis which suggests the Zr^{4+} preference for 7-fold coordination was corroborated experimentally. Hao *et al* studied the thermodynamic features of zirconia substituted

ceria by thermogravimetric analysis³⁴. The authors extracted the oxidation enthalpy and entropy for zirconia substituted ceria (ZSC) for ZSC having Zr content up to 20% by following a procedure outlined elsewhere for the oxidation reaction of $Ce_{1-x}Zr_xO_{2-\delta}^{43}$. The reaction during the oxidation step is:

$$\lim_{\alpha \to 0} \frac{2}{\alpha} M O_{2-\delta-\alpha} + O_2 \to \frac{2}{\alpha} M O_{2-\delta}$$
(1)

where M represents both Ce and Zr in solid solution. As α approaches 0, the activity of reactant and product solids are the same. Additionally, δ represents non-stoichiometry of the metal oxide. For the study presented in this article, oxygen is treated as an ideal gas. The Gibbs free energy for the oxidation step as a function of temperature is:

$$\Delta G^{\ominus}(T) = -RT ln K_{ox} = \Delta H_{ox}^{\ominus}(\delta) - T \Delta S_{ox}^{\ominus}$$
(2)

where R is the universal gas constant, T is temperature in Kelvin, K_{ox} is the equilibrium rate constant, ΔH_{ox}^{\ominus} is the standard enthalpy of oxidation, and ΔS_{ox}^{\ominus} is the standard entropy of oxidation. The authors argue that $K_{ox} = p_{0_2}^{*-1}$, where $p_{0_2}^{*}$ is oxygen partial pressure relative to standard state. Substituting this relationship into Eq. 2 gives an Arrhenius relationship:

$$lnp_{0_2}^*(\delta) = \frac{\Delta H_{ox}^{\ominus}(\delta)}{R} T^{-1} - \frac{\Delta S_{ox}^{\ominus}}{R}$$
(3)

where the temperature dependence of enthalpy and entropy are negligible. Thus a plot of $lnp_{O_2}^*$ vs. 1/T reveals the enthalpy and entropy as slope and intercept of the plotted line, respectively. Figure 3 plots the standard enthalpies and entropies of oxidation as a function of oxygen non-stoichiometry.



Figure 3: a) Standard enthalpy of oxidation and b) standard entropy of oxidation as a function of oxygen non-stoichiometry in Ceria-zirconia solid solutions. Insets are standard enthalpy and entropy plotted as a function of Zr content³⁴.

Both enthalpy and entropy decrease with increasing Zr content in the region of small nonstoichiometry (δ =0.2), and are both lower than the values obtained for pure ceria. This is attributed to the lower energy penalty of oxygen vacancy formation in Zr substituted ceria, due to its preference for 7-fold coordination. A decrease in entropy is ascribed to the preferential formation of oxygen vacancies next to Zr lattice sites, effectively ordering oxygen vacancies.

Chapter 1.5.2 Kinetics

In addition to materials design, manipulation of macroscopic architecture can improve the performance of catalyst materials. Originally, Umeda *et al* demonstrated superior propane conversion and rate capability of $Ce_{0.5}Zr_{0.5}O_2$ inverse opal over its porous, non-templated counterpart, as shown in Figure 4⁴. Aside from material selection, one of the main factors governing catalyst performance is surface area. In the case of inverse opals vs. non-templated materials, the non-templated materials have higher surface area. However, for gas-phase systems where mass transport considerations are crucial, accessible surface area is more important than overall surface area. The results in Figure 4 indicate a higher propane conversion rate and overall greater conversion for inverse opals when compared to non-templated materials. These results are due to increased mass transport through inverse opals.



Figure 4: Propane conversion percentage and rate as a function of temperature for $Ce_{0.5}Zr_{0.5}O_2$ pristine inverse opals, crushed inverse opals, non-templated powder, and SiO₂ blank⁴.

Although non-templated powders have high surface area, their porosity is very tortuous. Thus, a fraction of the surface area of non-templated powders is initially inaccessible to flowing gases. However, in the case of inverse opals the porosity is interconnected, and the gas path is not tortuous. Thus the mass-transport kinetics of the flowing gas is better for inverse opals than for non-templated controls.

Depending on the system gas flowrate, the oxidation reaction can either be mass transport or surface reaction limited. For a surface reaction limited process, inlet gases are flowing in excess, and energy requirements for heating are increased. For a mass transport limited process, the surface of the reactant solids are not saturated with gas, yet high fuel yield can still be observed in materials with ordered porosity.
Venstrom *et al* quantified the threshold between mass transport limited and surface reaction limited processes for the reduction of CO₂. For a horizontal packed bed of ceria particles, the maximum flow rate of CO₂ for mass transport limited kinetics during the oxidation step is 300 mL/min/g at $1500^{\circ}C^{44}$. Increasing flow up to 300 mL/min/g is accompanied by an increase in hydrogen production rate. At flow rates greater than 300mL/min/g, increasing flow rates have no effect on hydrogen production rate, as shown in Figure 5. At lower temperatures, this condition is met at lower flow rates, as the gas density is slightly higher.



Figure 5: CO production rate of ceria at 1500°C for flow rates up to 600mL/min/g⁴³.

Within the mass transport limited flow regime, inverse opals can have faster oxidation kinetics than non-templated powders.

Chapter 2 Ceria-Based Inverse Opals

Chapter 2.1 Colloidal Interactions Governing Crystal Formation

Originally, colloidal crystals were intriguing materials because of their ability to form photonic band gaps⁴⁵. Recently, colloidal crystals and their inverse structures (inverse opals) have become attractive material candidates in the fields of sensors^{46,47,48,49}, catalysis^{4,50}, battery electrodes^{51,52,53}, supercapacitors^{54,55}, and photovoltaics^{56,57,58,59,60}, to name a few.

In order to fully understand how a colloid assembles itself into a colloidal crystal, the nature of stable colloids must first be understood. Colloidal dispersions are defined as solutions containing particles ranging in size from 1 to 1000 nm, and are suspended and evenly distributed throughout the solvent matrix. A solution containing particles greater than 1000 nm is termed a suspension. A stable colloidal dispersion or suspension is defined by its resistance to aggregation over a significant period of time, as shown in Figure 6^{61} .

There are many forces dictating particle interactions within colloidal suspensions. For example, electrostatic repulsion arises from the charge present at the surface of particles in solution. The charge on the particle surface is the same sign for all of the same particles, and thus they are repelled. In addition, Van der Waals forces can act to attract the particles, and arises from temporary or permanent dipoles on the particle surface^{62,63}. Moreover, excluded volume repulsion accounts for the fact that no two particles can occupy the same space at any given time, and thus the particles are repelled from one another upon contact⁶⁴. Finally, entropic contributions cause such phenomena as Brownian motion, which keeps the particles constantly moving and in suspension⁶⁵. These forces can change with temperature, concentration, applied potential, pH, particle size and shape, and surface chemistry or charge, all of which can change the thickness and quality of the resulting colloidal structure.

In this work, colloids consist of polystyrene spheres with a narrow size distribution (<10% polydispersity) suspended in DI water or ethanol. These particles contain a surfactant or additive on their surface in order to charge the particle surface, causing them to effectively repel one another. This keeps the colloidal suspension stable and in solution, as shown in Figure 6.



Figure 6: a) stable colloid, b) unstable colloid, c) sedimented colloid

Chapter 2.2 Self-Assembly

Stable colloids can assemble themselves by mutual interaction forces into a larger functional material. The functional material of interest in this dissertation is termed a colloidal crystal. Colloidal crystals can self-assemble by many different methods, including sedimentation, centrifugation, and controlled drying on an interface⁶⁶.

The self-assembly method presented in this dissertation involves sedimentation by evaporation to produce colloidal crystals. Monodispersed beads in stable colloidal suspension will slowly selfassemble upon evaporation, leaving a thick, ordered colloidal crystal. With this method, thick colloidal crystals having large surface area are obtained, allowing for ease of process scale-up.

Chapter 2.3 Inverse Opal Fabrication Methods

Inverse opals are formed when the interstices of colloidal crystal are filled, and the colloidal crystal itself is removed by chemical, thermal, or mechanical means. A number of different combinations of template materials, assembly methods, and template removal methods have been explored, as shown in Table 1.

Material	Infused via	Template	Assembled via	Removed by
SiO ₂	Surfactant induced polymerization	Polystyrene spheres	Filtration	Calcination
TiO ₂	Hydrolysis	Polystyrene spheres	Centrifugation	Calcination
Polymers (DVB, EDMA, PMMA, etc.)	Heat or UV induced polymerization	Silica microspheres	Drying, pressing	Dissolution in HF
Graphite, glassy carbon, diamond	Pyrolysis, chemical vapor deposition	Silica microspheres	Sedimentation, drying, sintering	Dissolution in HF
Ni, Cu, Ag, Au, Pt	Seeding, electroless deposition	Silica microspheres	Deposition in vertical film	Dissolution in HF

Table 1: Examples of inverse opal fabrication step combinations⁶⁷

Chapter 2.4 Synthesis of Ceria Inverse Opals

In this dissertation, ceria-based inverse opal fabrication requires several discrete steps. First, polystyrene latex spheres must be either purchased or synthesized. The polystyrene spheres make up the colloidal crystal template, which is infiltrated with an appropriate precursor solution. Upon removal of the template at high temperatures, a crystalline ceria inverse opal remains. These inverse opals are subsequently characterized for their composition and quality of porosity.

Chapter 2.4.1 Latex Bead Syntheses

The first monodispersed polystyrene beads were synthesized by the Dow chemical company in 1947^{68,69}. From this work, authors were able to develop different techniques for monodispersed latex bead synthesis, such as emulsion polymerization⁷⁰, emulsifier-free emulsion polymerization⁷¹, seeded emulsion polymerization⁷², dispersion polymerization⁷³, and precipitation polymerization⁷³. Since the development of these techniques, monodispersed polystyrene beads have found their way into numerous applications, notably in the fields of photonics, biotechnology and biomimetics,^{74,75} and colloid science.

This work utilizes two types of polymer syntheses to achieve latex bead sizes from the submicron to micron size regime. For beads 300nm-800nm in size, an emulsifier-free emulsion synthesis was used, while a dispersion polymerization was used for beads $>1\mu$ m. High quality beads having a 1µm diameter were purchased in a 10wt/vol% aqueous suspension from ThermoFisher. Emulsifier-free emulsion syntheses are simpler to conduct than other synthesis methods, and yield monodispersed particles. Here, polydispersity is defined as the ratio of standard deviation of particle sizes to the average particle size. A monodispersed particle dispersion is defined as having a polydispersity <10%. Normally, emulsion polymerization syntheses utilize free radicals to initiate polymerization, and contain an oil phase, water phase, and a surfactant. With an emulsifier-free emulsion reaction, the oil and water phases are present, along with a dissolved salt in the solvent, but the addition of a surfactant would limit the particle size to ~500nm^{76,77,78}. The lack of surfactant, and also ionic strength of the solvent, allows for particle growth to proceed by coagulation. The monomer is oil soluble, the initiator is a water-soluble free radical initiator, and the solvent is water. In this case, hydroxyethyl methacrylate (HEMA) is added to the reaction in order to make the particle surface highly charged. A small amount of each drop of monomer is emulsified through stirring into the heated solvent, while the initiator remains above its radicalization temperature. The initiator is allowed to coagulate, and HEMA polymerizes on the surface of the particles. The hydroxyl group on the HEMA readily oxidizes to form a carboxyl group, which is negatively charged. The resulting beads are monodispersed, and their surfaces charged. The charged surface aids in the formation of ordered colloidal crystals upon sedimentation.

Here, we utilize a method developed by Reese and Asher⁷⁹ to synthesize beads for inverse opal templates. We were able to achieve 300-800nm beads with <10% polydispersity. For a representative synthesis, 51.25mL of deionized water, 15mL styrene, 50µL HEMA, 0.04g sodium chloride (NaCl), and 0.0275g potassium disulfide are added to a 3-neck flask. All styrene monomer used in polystyrene bead syntheses is first washed with sodium hydroxide (NaOH) for inhibitor removal. The styrene is placed in polystyrene centrifuge tubes and 1M NaOH is added until there are equal parts styrene and NaOH. Since styrene is immiscible in water, the mixture is emulsified using a vortex mixer (Vortex-Genie 2 Vortex Mixer, 120V), followed by a short 5 minute centrifugation at 1000rpm. The styrene is collected, the NaOH discarded, and the process

is repeated 2 times. The 3-neck flask is attached to the bottom of a water-cooled reflex column, which is connected to a Schlenk line, and a thermometer is inserted into the reactant solution through one of the rubber septum caps sealing two of the three necks of the flask. A schematic of the experimental setup is shown in Figure 7. A silicon oil bath that is placed on top of a hot plate is used to heat the flask, with a thermocouple inserted into the bath for temperature control. The solution is deaerated with 3 cycles of pulling vacuum for 3 minutes followed by purging with nitrogen gas for 2 minutes while stirring at 300rpm at room temperature. Once deaerated, the solution is kept under a blanket of nitrogen gas during the synthesis. The amount of NaCl was varied slightly to adjust final bead size. Next, the temperature of the solution is raised to 70° C, as indicated by the temperature reading on the thermometer inserted into the solution. Upon equilibration, the thermometer is removed, and the solution is injected with a solution of .0275g potassium persulfate, and 1.25mL DI water using a 3mL syringe and an 18g needle pierced through the septum. The reaction is allowed to proceed for 18 hours, after which a milky white suspension of polystyrene beads in water and residual styrene remains. The polystyrene beads are washed in DI water followed by centrifugation at 5000rpm for up to an hour for beads ~300nm. Washing is repeated at least 3 times, until the supernatant is clean and styrene-free.



Figure 7: Emulsifier-free emulsion reaction setup. 3-neck flask with solution in ambient atmosphere.

An SEM image of representative resulting 600nm beads are shown in Figure 8. Clearly, from this image one can see that the beads are monodispersed, and measurement of the beads confirms this, as shown in Table 2. For this work, 300nm, 500nm, 650nm, and 4300nm beads are used, and compared against commercially obtained 1000nm beads.



Figure 8: SEM image of monodispersed 600nm polystyrene beads, as- synthesized.

In order to synthesize beads larger than 1µm, a dropwise dispersion polymerization synthesis was utilized⁸⁰. With dispersion polymerization, the solvent dissolves monomer and not the polymer, and the initiator is soluble in the monomer. The polymerization reaction proceeds in the solvent/monomer phase, and small polymers form in solution until they form a critical molecular weight and precipitate out. From there, the dissolved monomer continues to polymerize on the surface of the precipitated polymers. A stabilizer is present in solution having one side which has an affinity for the polymer surface, and one with an affinity for the solution. The stabilizer covalently attaches to the surface of large particles creating a layer preventing agglomeration, thus allowing for monodispersed polymers to be formed. Here, the monomer used is styrene, the initiator is azobisisobutylnitrile (AIBN), the solvent is isopropanol, and the stabilizer is polyvinylpyrrolidone (PVP). For this synthesis, a 3-neck flask is charged with 1.25g PVP and

113mL isopropanol. The solution undergoes 3 deaeration cycles that consist of vacuum being pulled over the system followed by a nitrogen purge. During deaeration, a glass syringe is filled with 35mL styrene and 0.03g AIBN and placed on a syringe pump. Once deaerated, the solution is heated to 70°C, and a 12", 16g needle connected to the syringe is pierced through one of the septa on top of the 3-neck flask. The injection rate is set to 3mL/min, and the reaction is allowed to run for 15 hours. A milky white solution is present upon completion. The final solution is washed by diluting with ethanol, sonicating for 10 minutes, and centrifuging at 2000rpm for 10 minutes. The washing process is repeated at least 3 times to ensure that there is no residual monomer or small particles left in solution.

The beads used in this work are 4.3µm in size. This synthesis yielded large batches of beads with low polydispersity. Representative SEM image of beads are shown in Figure 9.



Figure 9: SEM image of 2.5µm monodispersed polystyrene beads, synthesized by dropwise dispersion polymerization

In addition to synthesized polystyrene beads, commercially obtained beads were used as inverse opal templates. These beads were also monodispersed, as shown qualitatively in Figure 10. Table 2 quantifies this monodispersity.



Figure 10: Commercially obtained 1µm polystyrene beads.

Beads obtained commercially and synthesized were measured for their size and polydispersity using SEM image analysis. Approximately 100 beads were measured for each bead size, and the results for several sizes are shown in Table 2. Polydispersity percentage was found by calculating the standard deviation, dividing by the average size, and multiplying by 100.

Table 2: Measured size and polydispersity for sub-micron and micron-sized polystyrene beads.

Synthesis method	Average size (nm)	Polydispersity (%)
Emulsifier-free emulsion	316	8.1
Emulsifier-free emulsion	603	5.5
Commercially obtained	1000	6.2
Dropwise dispersion	2500	5.7
Dropwise dispersion	4150	2.7

Chapter 2.4.2 Template Synthesis

Polystyrene opal templates were prepared by sedimentation of colloidal spheres in solution. For beads having diameters $\leq 1 \mu m$, this process consists of sonicating the bead suspension for ~1 minute, followed by dropcasting onto a flat surface. Round porcelain crucibles (Coorstek) were the substrate of preference for these beads, as they can be used for sedimentation, infiltration, and calcination. Beads were dried in ambient, allowing for slow sedimentation and formation of an ordered structure. Once dry, the newly formed colloidal crystal is placed into a drying furnace at ~50°C for at least 4 hours to ensure bonding between beads, and to encourage neck formation between beads. This step is crucial for the robustness of the colloidal crystal, and also for interconnectivity of the resulting inverse opal pores. An example of a colloidal crystal in a porcelain crucible is shown in Figure 11.



Figure 11: 1µm polystyrene bead colloidal crystal template in porcelain crucible.

Colloidal crystal templates made from beads $>1\mu$ m were prepared in several steps. First, the beads were coated in reduced graphene oxide (RGO) before sedimentation to improve connectivity of the inverse structure⁸¹. Dried polystyrene beads are added to the reduced graphene oxide in an

ammonium hydroxide/ethanol solution, which was previously prepared by modified Hummer's method⁸², to make a 100:1 polystyrene to RGO dispersion by weight. The dispersion is sonicated for 1 hour to ensure mixing between the RGO and polystyrene, and to allow the RGO to coat the PS surface. Next, the mixture is centrifuged at 2000rpm for 30 minutes to separate excess RGO from PS. The supernatant is disposed, and a black layer of excess RGO on top of the PS was washed away with isopropanol. The centrifuge tube was filled with isopropanol, and the solution was then vortexed and sonicated again to disperse the beads. At this stage, the beads are gray in color, as opposed to white, indicating that RGO has stuck the surface of the beads. The process of removing excess RGO and solvent with isopropanol, sonication, and centrifugation is repeated at least 3 times, until there is no longer a layer of excess RGO on the surface of the PS beads. The beads were drop-cast onto siliconized silica substrates (Hampton Research) and allowed to dry in ambient. The resulting colloidal crystal was finally dried in an oven at 105°C. Highlights of this process are shown in Figure 12, along with an SEM image showing PS beads coated in graphene.



Figure 12: a) Schematic of process to coat PS beads with RGO, followed by sedimentation of template onto a siliconized silica substrate, b) SEM image of PS beads coated in graphene.

Chapter 2.4.3 Ceria/Zirconia Precursor Synthesis

 $Ce_xZr_{1-x}O_2$ (x=0.9, 0.8, 0.7, 0.6) denoted zirconium substituted ceria, or ZSCX) powders were prepared according to a modified version of Hirano's method^{83,84}. Ammonium ceric nitrate ((NH₄)₂Ce(NO₃)₆, Acros Organics, 99%) and zirconyl chloride octahydrate (ZrOCl₂·8H₂0, Acros Organics, 98%) were dissolved in deionized water to make a 0.8M (Ce⁴⁺+Zr⁴⁺) aqueous solution. The ratio of (NH₄)₂Ce(NO₃)₆ and ZrOCl₂·8H₂0 are varied by weight to obtain the appropriate Ce⁴⁺ to Zr⁴⁺ ratio. Recipes for each solid are shown in Table 3.

	ZSC10	ZSC 20	ZSC 30	ZSC 40
$(NH_4)_2Ce(NO_3)_6(g)$	2.93	2.69	2.42	2.15
ZrOCl ₂ ·8H20 (g)	0.19	0.38	0.62	0.84
H ₂ O (mL)	20	20	20	20

Table 3: Precursor amounts used for ZSC syntheses with varying Zr content.

The solution was stirred at 150rpm and heated using a silicone oil bath at 105°C in an open vessel until dried, resulting in a dry ZSC solid. The solid was re-suspended in deionized water for use as the inverse opal precursor. Pure CeO₂ precursor was prepared using a cerium (III) chloride (CeCl₃·7H₂O, Sigma-Aldrich, 99%) methanolic solution⁸⁵. Typically, 2g CeCl₃ is dissolved in 3mL methanol, and stirred for at least 15 minutes at room temperature.

Chapter 2.4.4 Ceria Inverse Opal Syntheses

Appropriate amounts of ceria-based precursor were added drop-wise (10µL drop size, multiple rounds of infiltration) to the colloidal crystal templates and allowed to dry overnight at 60°C. The template/sol composite was heated at 1°C/min to 550°C and calcined for 1 hour, followed by annealing at 800°C for 1 hour (Barnstead Thermolyne, Type FB1400). A schematic of the overall inverse opal fabrication process is shown in Figure 13.



Figure 13: Inverse opal processing scheme. Inset of finished inverse opal in porcelain crucible showing opalescence.

Chapter 2.5 Characterization Methods

Chapter 2.5.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) images serve as the main indicator of ordered porosity within inverse opal structures. Up to 3 layers of inverse opal pores can be seen in high quality SEM images. An FEI Nova Nano 230 SEM equipped with environmental SEM mode is utilized for non-conducting ceria samples. 10kV accelerating voltage was used with a spot size of 3. Representative images of ZSC inverse opals having different sizes are shown in Figure 14.



Figure 14: ZSC20 inverse opals having a) 500nm, b) 1µm, and c) 4.3µm pore sizes, as-prepared.

Chapter 2.5.2 Electron Dispersive X-Ray Spectroscopy (EDS)

After synthesis of ZSC inverse opals, the composition, phase, and quality of microstructure must be verified. During optimization of materials synthesis, the actual composition was verified to match the nominal composition. First, energy dispersive X-ray spectroscopy (EDS) was used to confirm presence of Ce, Zr, and O in ceria-zirconia inverse opals. EDS spectra were taken in the Nova Nano 230 SEM at high vacuum, 15kV accelerating voltage, and spot size=4. Figure 15 shows the EDS spectra of a) ZSC0 and b) ZSC20. The Zr content in (b) is approximately 20 at%, which is the nominal value of ZSC20, as outlined in Table 4. However for accurate EDS characterization,

samples must be flat and polished. ZSC inverse opals are inherently rough, with topographical features spanning from the nm range for grains, micron range for pores, and millimeter range for particles. For this reason, EDS is used as a qualitative measure to verify the presence of elements, and to detect potential contaminants.



Figure 15: EDS spectra of a) ZSC0 and b) ZSC20 as-prepared inverse opals.

Table 4: Comparison of nominal and EDS calculated Zr content in ZSC.

Nominal composition	Powder control EDS composition	Inverse opal EDS composition
CeO ₂	CeO ₂	CeO ₂
$Ce_{0.8}Zr_{0.2}O_2$	$Ce_{0.81}Zr_{0.19}O_2$	$Ce_{0.85}Zr_{0.15}O_2$
$Ce_{0.6}Zr_{0.4}O_2$	Ce _{0.67} Zr _{0.33} O ₂	Ce _{0.66} Zr _{0.34} O ₂

In order to verify that composition is independent of macroscopic architecture, EDS was done on ZSC0, 20, and 40 powder controls and inverse opals. As expected, the Zr content of nontemplated controls correlate well with the Zr content of inverse opals in all cases.

Chapter 2.5.3 X-Ray Diffraction (XRD)

In order to verify the phases present in the inverse opal, *in situ* powder XRD was performed on various ZSC powders, as well as *ex situ* powder XRD on inverse opals and powders. Tetragonal phase formation is most obviously indicated by the appearance of a shoulder near the (111) and (220) reflections. XRD showed no evidence of any tetragonal phase formation in pure ceria, and ZSC10, and in this work, materials of interest have at least 20 at% Zr. *Ex situ* powder XRD patterns for ZSC20, ZSC30, and ZSC40 after annealing at 1100°C are shown in Figure 16. Although tetragonal phase formation is not detected in ZSC20, phase segregation into Zr-rich tetragonal and Ce-rich cubic phases begins to occur when Zr content is \geq 30 at%. *In situ* XRD of ZSC powders heated from room temperature to 1200°C is plotted in Figure 17 in order to determine the onset of tetragonal phase formation. From these data, tetragonal phase is not present in as-prepared materials with Zr content between 0 and 30 at%. However, it is unclear whether the asymmetry of the (111) peak in ZSC40 is caused by broadening caused by small crystallite size, or tetragonal phase formation. At 1200°C, tetragonal phase formation can be observed for Zr content \geq 20 at%. We expect ZSC20 to maintain the cubic structure at 1100° C, but at 1200° C, the system approaches the cubic phase boundary on the CeO₂-ZrO₂ phase diagram (Figure 2 a).



Figure 16: Powder XRD patterns of ZSC20, 30, and 40 inverse opals annealed at 1100°C for 12 hours. Black lines indicating cubic phase reference, gray lines indicating tetragonal phase reference.



Figure 17: *In situ* XRD patterns of ZSCX powders a) as-prepared and at room temperature, and b) heated to 1200°C in air. Arrows point to "shoulders" on cubic phase peaks, indicating evidence of tetragonal phase formation.

Chapter 2.5.4 Raman Spectroscopy

Raman spectroscopy is necessary for detection of subtle changes in the oxygen lattice such as pseudocubic phase formation. The metastable t" phase is characterized by a distortion in the

oxygen sublattice, while cation positions remain unchanged, essentially resulting in an oxygen defective cubic structure. For this reason, the psuedocubic t" phase in undetectable using XRD. A schematic of oxygen vacancy and pseudocubic phase defects are shown in Figure 18. The pseudocubic phase is known to have higher oxygen storage capacity and mobility than that of the cubic phase.



Figure 18: Cubic ceria having a) oxygen vacancy defects and b) pseudocubic phase distortions. These distortions in the anion sublattice are easily detected through Raman spectroscopy.

Upon increasing Zr content, additional tetragonal (t' and t) phases form, which are characterized by lattice parameter ratio c/a=1.1 and 1.4, respectively. The oxygen storage capacity of tetragonal ceria suffers significantly when compared to cubic ceria^{40,86}. Tetragonal phase formation is suppressed in nano-sized grains, but upon annealing at high temperatures this benefit

is lost. Raman spectroscopy was performed using a Renishaw InVia spectrometer, equipped with a 514nm green laser. The expected cubic phase band occurs at $464cm^{-1}$, while defect peaks associated with oxygen vacancies and tetragonal t" phase occur at approximately 600 cm⁻¹ and $300cm^{-1}$, respectively. At high Zr content, 6 tetragonal peaks appear, which overlap with the cubic peak, designated by 1-6 in Figure 19. Raman spectra from literature of ZSCX materials when 0 < X < 0.9 are shown in Figure 19³³. Both an increase in oxygen vacancy concentration, as well as pseudocubic phase concentration, are observed with increasing Zr content.



Figure 19: Raman spectra of $(1-x)CeO_2-xZrO_2$ samples annealed at 800°C. Peaks 3, 4, and 5 are associated with the pseudocubic phase, cubic phase, and oxygen vacancies, respectively when Zr concentration is low. At high Zr concentration (see x=0.9), peaks 1-6 are associated with the tetragonal t phase³³.

Chapter 3 Quantification of Inverse Opal Thermal Structural Stability

Chapter 3.1 Motivation

Previous authors have identified thermal operating limits for different inverse opals, however, these studies have been largely qualitative.^{87,88,89} For example, pure ceria and Zr-doped ceria inverse opals underwent isothermal redox cycling at 825°C. Through qualitative scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses, and using the human eye as a tool for recognition of ordered porosity, it was found that increasing Zr doping stabilized macroporous structures. All ZDC compositions maintained their respective structures under these conditions⁸⁷. In addition, Denny et al. evaluated the suitability of tungsten based inverse opals for thermionic emission applications. In this study, structural changes were clearly observed using *in situ* transmission electron spectroscopy, resulting in qualification of W/Mo inverse opals up to 1000°C; an appropriate temperature for thermionic operation^{88,89}. Although these studies establish inverse opal limitations, they do not offer prognostic information crucial to the lifetime considerations of practical applications

A vast amount of literature has been dedicated to quantification of the degree of ordered porosity in recent years, but is limited to low temperature applications. In particular, pore ordering and quality of anodic aluminum oxide porosity related to synthesis conditions has been of interest^{90,91}. There are currently no studies dedicated to quantifying the preservation of ordered porosity at elevated temperatures. Here, we applied quantitative image analysis techniques developed previously⁹² to study the effect of increasing zirconium concentration in ceria towards stabilizing inverse opal structures. By analyzing the fast Fourier transforms (FFT's) of SEM images, we extract a metric, named the reciprocal space order parameter γ , which is used to

measure the degree of order in the inverse opal. From these order parameters, the limits of cycling conditions for these materials is established.

Chapter 3.2 FFT methodology

The fast Fourier transform (FFT) is described by equation 1:

$$X(k_x, k_y) = \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} x(n_1, n_2) e^{-2\pi i \left(\frac{k_x n_1}{N_1} + \frac{k_y n_2}{N_2}\right)}$$
(1)

Where $x(n_1,n_2)$ is the array of brightness values and k/N is the spatial frequency. To compute the FFT, the fft2(X) function in Matlab was implemented. The image is converted to grayscale, a threshold applied, and cropped to remove the confounding information bar. The one-dimensional discrete Fourier transform (DFT) is computed first for each column, and subsequently computed for the row of each result. This results in a circular convolution, and the FFT data has the same dimensions as the original image. Next, Y=fftshift(x) is used to move the zero frequency component to the center, and the absolute value is taken in order to remove the imaginary values from the analysis. The absolute value is the intensity value seen in the final FFT image⁹³:

$$I(k_x, k_y) = |X(k_x k_y)| \qquad (2)$$

If the image contains spatial order, this will result in an array of spots similar to a diffraction pattern. The spots closest to the zero frequency average brightness value, which is at the center of the FFT image, represents the average brightness of the image, while the spots nearest to the zeroth frequency value represent the lowest frequency occurring order. For this study, these are the data of interest. The sum of the FFT along an axis of symmetry is taken by rotating the image and summing the columns of the resulting FFT (Figure 20).



Figure 20: a) Typical ZDC20 1µm inverse opal SEM image with threshold applied, b) shifted FFT image, c) rotated FFT image, d) sum of FFT image brightness along x-axis (matrix columns).

Chapter 3.3 Image Analysis

The Fourier transform of real space images was calculated in Matlab using the FFT2⁹⁴ function, as described by Kaatz. Here, a discrete Fourier transform converts real space image brightness to intensity values of a reciprocal space image⁹².

The sums of FFT's across chosen lines of symmetry (or random lines when no line of symmetry exists) found using Matlab are plotted as intensity vs. pixel distance from center, and can be resolved into peaks for images of ordered porosity. Within this plot the zeroth order peak represents the average brightness, while the first order peak describes long range order.

Here, we define a reciprocal space order parameter γ ,

$$\gamma = \frac{l_{I_0}}{\sigma} = \frac{l_r}{\sigma} \quad (5)$$

where I is the 1st order peak intensity, I_0 is the normalized zeroth order peak intensity, I_r is the relative intensity (I/I₀), and σ is the estimated full width at half maximum (FWHM) of the first order peak.

The spatial order parameter extracted from these FFT analyses is defined as the ratio of peak intensity of the sum across the "spots" in the correlated image and the full width at half maximum (FWHM) of the peak normalized by the total width of the image in pixels.

In order to calculate the spatial order parameter γ , the peak intensity and full width at half maximum (FWHM) must be extracted. To do this, the findpeaks function in Matlab was used, and the standard deviation of each peak was taken to estimate the FWHM. The peak minimum was subtracted from the peak maximum to find the height.

Chapter 3.4 Experimental

 $Ce_xZr_{1-x}O_2$ (x=0.9, 0.8, 0.7, 0.6, denoted zirconium doped substituted ceria, or ZSCX) powders were prepared according methods described in Chapter 2.

Polystyrene opal templates were made by sedimentation of colloidal spheres in solution. Commercially available 1 μ m polystyrene beads in aqueous dispersion (ThermoFisher, 1 μ m, 10% wt/vol) were used in addition to 300nm, 650nm and 4.3 μ m beads, which were synthesized (Ch. 2)^{79, 80}. Beads larger than 1 μ m were coated in reduced graphene oxide before sedimentation to improve connectivity of the inverse structure.⁸¹ The beads were drop-cast onto porcelain crucibles (sub-micron beads), or siliconized silica substrates (4.3 μ m beads) and allowed to dry ambiently. The resulting colloidal crystal was dried and calcined according to procedures in Ch. 2.

Thermal Treatment: Ceria-zirconia inverse opals with various compositions and pore sizes were assessed for their thermal stability. ZSCX (X=0, 10, 20, 30, 40) materials having a 1µm

nominal pore size were heated at 1000°C and 1100°C in air for 1, 6 and 12 hours. In addition, ZSC20 inverse opals having 650nm, 1 μ m, and 4.3 μ m nominal pore diameters were heated in air to 1000°C for 1, 6, and 12 hours. All samples were air quenched upon completion of thermal treatment.

Inverse opal macrostructures were isothermally cycled at 800°C to evaluate their robustness during redox. ZSC20 inverse opals having 300nm, 650nm and 1µm nominal pore sizes were subjected to isothermal treatment under a chemically cycled gas. This process is explained in detail in Chapter 5. The total dwell time at 800°C was approximately 12 hours. Control samples having the same inverse opal morphologies and pore sizes of those treated under chemically cycled gas were heated to 800°C under a fixed gas (air) for 12 hours.

Characterization: Powder x-ray diffraction (XRD) was performed using a tabletop powder xray diffractometer (Rigaku MiniFlex, 300W) using a Cu K α source (λ =1.54Å) before and after heat treatment for phase verification. Scherrer's equation was used to estimate crystallite size (26). Raman spectroscopy (Renishaw, 514nm) was used to verify subtle changes in the oxygen lattice such as vacancy formation and emergence of the pseudocubic (t'') phase. SEM was performed using the FEI Nova Nano field emission instrument. Most images were taken in low vacuum mode (10KV, 60Pa), otherwise samples were sputtered with gold. Inverse opals were crushed and deposited onto sample stubs to ensure that the ordered porosity was viewed throughout the entire sample. The field of view for this analysis contains approximately 70 pores for micron sized inverse opals, and 250 pores for sub-micron inverse opals.

Chapter 3.5 Compositional Effects on Thermal Stability

Representative inverse opal macrostructures, prepared using 1 µm PS template beads, and their associated FFT sums are shown in Figure 21. The as-synthesized ZSC20 is highly ordered, as evidenced both by simple visual inspection of the SEM image, and the corresponding FFT profile. The FFT intensity profiles contain sharp or broad peaks for ordered and disordered structures, respectively. The intensity of the first order spot in the 2-D FFT image correlates well with the degree of structural order. ZSC20 inverse opals which have undergone moderate annealing reveal ordered structures which correspond to sharp peaks in the FFT sums (Fig. 21g). As heat treatments are applied, structural changes are visually apparent in both the SEM and FFT images, while more subtle changes are displayed using the FFT analysis. From this visual analysis we obtain a point of reference for defining order and disorder for use in the quantitative analysis.



Figure 21: a-c) SEM images of a) Ce_{0.8}Zr_{0.2}O₂ (ZSC20) as-synthesized, b) ZSC20 after annealing at 1100°C for 12 hours, c) ZSC10 after annealing at 1100°C for 12 hours. d-f) 2-D FFTs corresponding to SEM images. g-i) Sum of 2-D FFTs across a line of symmetry (in the case of i., across any line) corresponding to 2-D FFTs. First-order peaks of intense pixel brightness are indicative of ordered porosity. The center peak (zeroth order) indicates image average brightness, and is an artifact of the analysis in all cases.

SEM images with accompanying FFT patterns of pristine ZSCX inverse opals and their degradation with increasing temperature are shown in Figure 23. These samples were prepared using the same polystyrene bead size of 1 μ m and thus possess the same nominal pore diameter of 1 μ m. The samples were annealed at 1000°C and 1100°C for up to 12 hours to mimic thermal cycling conditions. Since the addition of zirconia is known to suppress grain growth by a dopant drag mechanism^{95,96}, it is not surprising that compositions with greater Zr⁴⁺ content maintain the inverse opal architecture as evidenced by both visual observation and by the presence of spots in the FFT pattern.



Figure 22: SEM images FFT pattern insets of ZSC0 (a-c), ZSC10 (d-f), ZSC20 (g-i), ZSC30 (j-l), and ZSC40 (m-o) inverse opals (a,d,g,j,m) as-synthesized, (b,e,h,k,n) annealed at 1000°C for 12 hours, and (c,f,i,l,o) annealed at 1100°C for 12 hours, showing the structural response to thermal treatment for varying composition.

The results in Figure 22 show that the thermal stability of the inverse opal architecture has a strong composition dependence. The pores of ZSC30 and ZSC40 inverse opals remain entirely ordered after annealing at 1100°C for 12 hours. ZSC20 inverse opals are not quite as robust as they have only limited areas maintaining order at 1100°C. However, ZSC20 does maintain complete ordered porosity at 1000°C for an extended annealing time. Pure ceria and ZSC10 coarsen significantly and lose order at 1000°C. Although incorporating zirconia inhibits coarsening and increases overall catalytic activity^{34,35}, it should be recognized that the full advantage of Zr^{4+} additions in the ceria lattice depends on device operating parameters.

The FFT order parameter (Eqn. 5) is sensitive to the variations in composition, thermal treatment and heat treatment time. Figure 24 plots γ versus time held at elevated temperatures, and shows a decrease in γ with annealing time. This is consistent with the SEM images in Figure 23. In order to assign values of γ which are representative of the observed thermal stability, we correlated the range of γ values with various microstructures. The samples which maintain ordered porosity at 1100°C, ZSC30 and ZSC40, have $\gamma >4$, suggesting that this value offers a good indication of macroscopic periodicity. In addition, the results for ZSC0, ZSC10 and ZSC20 suggest that $2 < \gamma <4$ is associated with the loss of periodicity. That is, this range represents a transition between ordered porosity and one which exhibits decreasing order. Finally, our results indicate that $\gamma <2$ has random porosity. From this analysis, we are able to monitor compositional systems which lose periodicity as a function of annealing time and those that maintain it over time.

The extent of zirconium substitution has a distinct effect on the thermal stability of the porous architecture. The results shown in Figure 25 and 26 show that ZSC20 is able to retain an ordered inverse opal architecture at 1000°C for an extended period of time. Although this is an improvement over previously established stability limits for these materials, this temperature is

not adequate for the ideal temperature swing from 800°C to 1500°C for thermochemical cycling of pure ceria^{4,44}. Even inverse opals with Zr content of 40% show a gradual loss of periodicity at 1100°C (Figure 23a). An interesting feature for the pure ceria inverse opal is that its order parameter is noticeably smaller than the order parameters for zirconium substituted specimens in Figure 23. This decreased order parameter is most likely due to the different precursor used in the synthesis of CeO2 (cerium chloride), vs. ZSC (ceric ammonium nitrate). Moreover, ZSC10 experiences a steep drop in γ after 1 hour at 1000°C and 1100°C. At these temperatures, ZSC10 undergoes coarsening that does not occur at 800°C. These results further emphasize the importance that even small zirconium additions have on thermal stability.



Figure 23: Order parameters for ZSC inverse opals annealed at a) 1100°C and b) 1000°C. Samples with γ <2 are considered completely disordered. This threshold is indicated by dotted line. The shaded region at 2< γ <4 represents the transition to disorder region.

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The relationship between coarsening and retention of the inverse opal architecture at elevated temperature is further shown by the results presented in Figure 24. In this figure, the dependence of γ on crystallite size is shown for as-prepared samples and for the same sample after annealing at 1100°C for 12 hours. The compositions range from pure ceria to ZSC40. The change in γ for the former is dramatic, from an ordered structure ($\gamma \sim 7$ with d ~ 20 nm) to a completely disordered structure ($\gamma \sim 1$ with d ~ 80 nm). For ZSC40, γ decreases from 11 to 5 but nonetheless remains highly ordered, while crystallite size changes only slightly (8nm to 13nm). The amount of Zr is the key parameter which determines the relation between coarsening and the ability of inverse opals to maintain their structures. Coarse grains allow facile crack propagation along grain boundaries, and thus make inverse opals more susceptible fracture^{97,98} and loss of order.


Figure 24: a) Powder XRD patterns for ZSC20, ZSC30, and ZSC40 inverse opals as-synthesized and annealed at 1100°C for 12 hours. Lines indicate peak locations for tetragonal $Ce_{0.86}Zr_{0.14}O_2$ reference (JCPDS 00-038-1437). b) Gamma as a function of zirconium dependent grain size for ZSC as-synthesized (closed symbols) and annealed at 1100°C (open symbols). Crystallite size for ZSC10 from reference 96.

Another important effect associated with the addition of zirconia to ceria is that undesired tetragonal phases can form^{29,33,43}. Nonstoichiometric cerium oxide has high oxygen storage capacity and ion mobility due to a large oxygen vacancy concentration and the openness of the tetrahedral site of the cubic fluorite phase^{5,6,29}. In addition, the Ce⁴⁺ and Zr⁴⁺ ionic radii difference distorts the cubic lattice, making defects energetically favorable⁶. Strains associated with Zr⁴⁺ content accommodate larger Ce³⁺ ions. According to the bulk ceria-zirconia phase diagram, the pseudocubic phase (t^{*}) appears as Zr content approaches ~12%. This is indicated in Raman spectroscopy by the appearance of a peak at ~300cm^{-1 33}. Raman spectroscopy (Renishaw, 514nm) was used to verify subtle changes in the oxygen sublattice such as vacancy formation and emergence of the pseudocubic (t^{*}) phase. Figure 25 shows the Raman spectra of ZDC20 inverse opals annealed at 1100°C for 0.5 and 12 hours.



Figure 25: Raman spectra of ZDC20 1µm inverse opal a) as-synthesized, and annealed at 1100°C for b) 0.5 hours and c) 12 hours. Defect band, cubic phase band, and defect band located at 1, 2, and 3, respectively.

The main cubic phase vibrational mode peak occurs at 464 cm⁻¹ for pure ceria, while the defect band is at 600 cm⁻¹, and the pseudocubic phase band appears at 307 cm⁻¹, designated by 2,1, and 3 in Figure 25, respectively²⁹. The cubic peak position is shifted slightly due to the addition of zirconia, and shift of the cubic peak to higher wavenumbers with annealing occurs due to crystallite growth. This phenomenon is likely attributed to phonon confinement in small nanoparticles, in addition to lattice expansion, and these effects disappear as the nanocrystals grow⁹⁹. The defect line is indicative of oxygen vacancy concentration, and is associated with the pseudocubic phase. In this phase, cation positions remain unchanged and oxygen positions are slightly shifted from their locations in the cubic lattice.



Figure 26: Raman spectra of ZDC inverse opals annealed at 1000°C and 1100°C for 1 hour with a) 0, b) 10, c) 20, d) 30, e), 40 atomic percent zirconium.

None of the ZDC samples annealed at 1000°C showed evidence of tetragonal phase formation, as shown in Figure 26, which would be indicated by peaks in addition to 1, 2 and 3, defined in Figure 26. The Raman spectra of ZDC30 and ZDC 40 did, however, contain small broad peaks at 307 cm⁻¹ and 600 cm⁻¹, indicating the emergence of the defective pseudocubic phase. ZDCX inverse opals annealed at 1100°C for 1 hour are shown to contain defective pseudocubic phase where X>10. However, undesired tetragonal phases begin to develop for X>30, as indicated by the presence of additional peaks ~260 cm⁻¹. Longer annealing times may increase the amount of pseudocubic phase for ZDCX materials, but has the adverse effect of increasing crystallite size.

There exists a balance between tetragonal phase formation and structural stability for zirconium in ceria. Maximum oxygen storage capacity occurs when ceria contains 15-20 at% zirconia^{33,34,100}. At this loading, zirconium causes a strain in the cubic lattice which accommodates Ce^{3+} formation without the appearance of tetragonal phases. However, lower zirconium doping does not substantially mitigate coarsening effects, and consequently, delicate architectures such as inverse opals will lose periodicity at elevated temperatures. For this reason, the decrease in order parameter with increasing crystallite size, shown in Figure 24, is indicative of the relationship between coarsening and the ability of inverse opals to maintain their structures. Coarse grains make inverse opals more susceptible to crack propagation and breakage as a result of thermal or mechanical shock, typical of thermochemical multi-temperature cycling procedures¹⁰⁰. Powder XRD patterns for ZSC20, 30, and 40 after annealing at 1100°C for 12 hours (Figure 24a) show peak splitting, indicating formation of a second phase with smaller lattice parameter for zirconia content greater than 20 at%¹⁰¹. The shift of the (100) reflection at 29° to lower 20 and the appearance of a shoulder at 30° points to a segregation of material into zirconium rich tetragonal and zirconium poor cubic oxides. Appropriate reference patterns for cerium rich cubic and zirconium rich tetragonal phases are included in Figure 24a. The maximum zirconium content for Zr doped ceria inverse opals in operation is therefore 20 atomic percent.

Chapter 3.6 Pore Size Effects on Thermal Stability

During thermochemical cycling, reactants are fed to the catalyst surface via the flowing gas phase. Rapid flow is central to fast kinetics and can potentially be rate limiting. In order for the gas to have sufficiently high diffusivities through pores at the nano to micro scale, molecular flow through the windows connecting each pore is desired. Molecular, or bulk flow diffusivities are

normally an order of magnitude greater than those associated with Knudsen flow.^{132,134} Therefore, based on the calculations contained in Appendix A, a pore diameter larger than 1µm should improve flow characteristics dramatically. For this reason, we initiated efforts at fabricating large pore inverse opals. The synthesis of such materials with pore diameters above 1 µm has been a challenge due to the complex methods necessary for synthesis of large (>3µm) monodispersed polystyrene bead colloidal suspensions¹⁰², as well as a tendency for the suspension to settle. Here, we successfully synthesized polystyrene beads as large as 4.3 µm which enabled us to prepare large pore inverse opals capable of supporting molecular flow. An added benefit of large diameter inverse opals is that the material offers better thermal stability compared to in-verse opals with smaller pores ($< 1\mu m$). The pore radius of curvature is much larger, and thus the surface energy is less for large pore materials¹⁰³. The change in γ as a function of polystyrene template diameter at 1000°C is shown in Figure 27 for ZSC20 inverse opals with template diameters ranging by nearly an order of magnitude. Inverse opals with a 500 nm pore diameter rapidly lose order at 1000°C, although this temperature is suitable for ZSC20 inverse opals with pore sizes $>1 \mu m$, as shown in Figure 23(b). This behavior is likely due to the small radii of curvature possessed by nano-sized pores which, in combination with short diffusion distances, lead to a greater likelihood of densification and pore collapse.



Figure 27: Order parameter as a function of time for 500, 1000, and 4300nm pore size inverse opals annealed at 1000°C. Inset of pore "window" which allows gas flow between pores.

Chapter 3.7 Chemical Cycling Effects

Table 5 shows a comparison of γ values for ZSC20 inverse opals as-synthesized (γ_0), after isothermal treatment (*vide infra*) at 800°C under a chemically cycled gas (γ_{cc}), and after isothermal treatment at 800°C under a fixed gas (γ_{fg}). Materials heated under a fixed gas (air) act as controls, and are comparable to results from the thermal stability experiments described above. Inverse opals subjected to chemically cycled gas were expected to lose ordered porosity due to volume expansion during reoxidation and shrinkage during reduction. However, all structures maintained ordered porosity. Although gamma values are decreased after heating in all cases, as indicated by γ_{cc} , and γ_{fg} , respectively, these values of gamma are still well within the established limits of order. Minimal loss of order was also observed during thermal stability tests for ZSC20, as indicated above, and is attributed to coarsening effects. Figure 28 shows ZSC20 inverse opal with 300nm pore size as-synthesized, and after cycling. It is particularly surprising that even the 300nm diameter inverse opal survived these treatments. As indicated above, small pores are expected to collapse faster than large pores, due to small pore radii of curvature and shorter diffusion distances. For inverse opals having 1µm pore size, thermal stability experiments indicate that ordered porosity is maintained at 1000 °C under a fixed gas composition, while cycling experiments indicate negligible effects of chemically cycled gas on macrostructural architecture. This points to an opportunity to further increase the cycling temperatures for templated ceria, without any loss of the benefits associated with ordered porosity.

Table 5: Order parameters for ZSC20 inverse opals before and after thermal treatment.

Template size (nm)	γο	γcc	γ_{fg}	
300	8.1	4.2	5.9	
650	7.3	4.6	4.5	
1000	9.8	6.2	7.5	



Figure 28: ZSC20 inverse opal with 300nm pore size a) as-synthesized and b) after isothermal heating at 800°C under a chemically cycled gas.

Chapter 3.8 Conclusion

In this work, a method for quantitatively describing the degree of pore ordering was applied to inverse opal architectures. By comparing SEM images to 2-D sums of image FFT's, an order parameter γ was defined. Here, γ >4 indicates full ordered porosity, while complete loss of ordered porosity is apparent when γ <2. Using this definition for the degree of order, ceria inverse opals with at least 20 atomic percent zirconium were found to maintain order up to 1000°C for 12 hours. In addition, this Zr content resulted in a pseudo-cubic defect structure that successfully avoided tetragonal phase formation.

In order for inverse opals to lead to improvements in fuel production efficiency, two important features must be achieved; retention of ordered porosity at elevated temperature and the development of large pore inverse opals which support molecular flow for gas flow reactivity. Both features have been evaluated here as inverse opals templated with 4.3 µm diameter polystyrene spheres were prepared. The resulting materials exhibited far better stability at 1000°C compared to 500 nm beads. We expect that ZSC20 inverse opals with pores ~5µm are robust and will maintain structures at temperatures upwards of 1000°C, allowing more efficient operation and thereby improving overall fuel productivity

Chapter 4 Coarsening of Inverse Opals

The influence of ordered porosity on coarsening and high-temperature degradation of ceriabased inverse opals is reported in this section. Coarsening is most easily revealed by observation of grain growth in materials. Existing grain growth models are applied to inverse opals and nontemplated materials by using *ex situ* TEM grain size measurements. In addition, a model for structural degradation of inverse opals is presented and verified. Lastly, structural changes as observed by *in situ* SEM are related to microstructural changes, and found to be scalable.

Chapter 4.1 Motivation for Study

Materials used for thermochemical hydrogen production are subjected to high temperatures (>1000°C), quick cooling and heating, as well as cyclic redox environments. Inverse opals in solar thermochemical devices may be subjected to thermal stresses induced by temperature gradients within large inverse opal pieces and thermal cycling, as well as strains induced by redox cycles. However, the majority of changes within the inverse opal structure occur due to grain growth as a result of high temperature exposure.

A fundamental understanding of inverse opal high temperature degradation mechanisms is crucial for further material optimization. By knowing the dominant grain growth mechanism, such as surface diffusion, lattice diffusion or grain boundary diffusion, we can find ways to mitigate coarsening effects, while balancing other desirable material characteristics. For example, aliovalent dopants such as Gd_2O_3 increase ionic conductivity of ceria for solid oxide fuel cell (SOFC) applications¹⁰⁴ and can increase oxygen storage capacity by promoting oxygen vacancy formation. Gd^{3+} in ceria increases grain boundary mobility at low doping levels (0.1%), but decrease grain boundary mobility at high doping levels (1-35%)⁹⁶.

Chapter 4.2 Coarsening Theory: Existing Models

Grain growth occurs in ceria-based inverse opals by coarsening. Grain coarsening is characterized by an overall increase in grain size, with the total number of grains decreasing in time. Figure 29(a) shows a qualitative mechanism of grain growth by grain boundary migration. Particles of different sizes attach, and necks form between them, followed by grain boundary movement towards the smaller particle, effectively causing grain growth of the larger particle. The bigger the size difference between the two connecting particles, the greater the radius of curvature of the grain boundary, and thus the greater driving force for grain boundary migration. Figure 29 (b) further shows this phenomenon occurring by surface diffusion in a cluster of grains. Again, grain boundaries migrate towards smaller grains while larger grains grow. In addition, for porous materials, coarsening occurs separately from sintering, as pore size increases simultaneously with grain size. For sintering processes, porosity decreases, and densification occurs. Materials with high porosity have different grain growth kinetics than their dense counterparts. Porosity can hinder grain coarsening, as neck growth must occur before grain boundary migration¹⁰⁷. Additionally, if surface diffusion is found to be the dominant mechanism governing grain growth, additives can slow this process, further extending the lifetime of inverse opal structures.



Figure 29: a) Grain growth by neck growth followed by grain boundary migration b) grain growth in a cluster of grains by surface diffusion¹⁰⁵

Grain boundary mobility is related grain boundary velocity and driving force for grain boundary movement by:

$$v \propto M * F \tag{1}$$

where M is grain boundary mobility, v is grain boundary velocity, and F is driving force¹⁰⁶. The driving force for grain boundary mobility increases as the radius of curvature of the grain boundary decreases. Grain boundary mobility of high-angle grain boundaries can be further estimated:

$$M = \frac{bv\Omega}{kT} exp\left(-\frac{Q}{kT}\right) \qquad (2)$$

where b is burgers vector of the dislocation at the grain boundary, v is jump frequency, k is Bolzmann's constant, T is temperature, and Q is activation energy for grain boundary movement.¹⁰⁷

The force acting on the surface of a curved grain is related to surface tension by

$$F \propto \frac{\gamma}{r} \propto \frac{2\gamma}{D_{ave}}$$
 (3)

where γ is surface tension, r is the radius of curvature of the grain, and D_{ave} is mean grain size, which will simply be named D. Two grains which are touching, and have different size, will have different radii of curvature. Thus, the forces acting on the grain boundaries will be different, and tend to take shape of the grain with the greater force acting upon it (smaller grain). Under ambient conditions, these grains are metastable, but when given enough energy in the form of heat, the grain boundary moves towards its center of curvature, and the larger grains grow at the expense of the smaller ones. This is the reason that grains with convex grain boundaries tend to grow, while those with concave grain boundaries tend to shrink. The only cases in which grain boundary forces are balanced, and thus grain boundaries will be frozen, even at high temperatures, are when grain boundaries are planar, or curved with equal radii of curvature in opposite directions, as shown in Figure 30(b) and (c).¹⁰⁷



Figure 30: a) A cylindrical grain boundary with curvature r and surface tension γ , acted on by force γ/r , b) planar boundary with r= ∞ , and c) doubly curved boundary with balancing forces (adapted from Porter¹⁰⁷)

Grain boundary radius of curvature is directly proportional to grain size, and thus the driving force for grain growth is proportional to surface tension and inversely proportional to grain size ^{108,109,110}. For all grain-growth processes, the velocity of the grain boundary is also equal to:

$$v_{ave} = \alpha M \frac{2\gamma}{D} \cdot \frac{dD}{dt} \quad (4)$$

Where α is a proportionality constant. When this equation is integrated with D at time 0=D_o, we are left with the classical parabolic growth model:

$$D^2 - D_o^2 = Kt \quad (6)$$

where K=4 α M γ . If D>>D_o, D_o can be neglected, and a more generalized form of the grain growth equation is used:

$$D^n = 2Kt \quad (7)$$

Where n=2, and K is a rate constant. This relationship was first developed by Beck, Burke, and Burke and Turnbull^{111,112,113}, and is based on an assumption that grain growth is parabolic, and is inversely related to grain size^{114,115,116,117,118}. This relationship describes grain growth well in pure, single-phase metals. However, for many technical materials, n deviates from 2, and is usually between 2 and 4^{119} . Although the meaning for this deviation is not well understood, one explanation is that mobility does not vary linearly with driving force for various reasons. For Ostwald ripening and diffusion controlled mechanisms, n=3¹²⁰, and for interface controlled mechanisms n=2.

Until recently, values of n>4 were thought to have no physical meaning. However, a mechanism of grain boundary relaxation has been proposed for nanocrystalline materials, and for this process n can approach 10^{121} . While grain growth exponent, n, gives us a general idea of grain growth behavior, further analysis is necessary to narrow down the actual mechanism.

Höfler and Averback modified Burke's original equation to accommodate deviations from ideality, where grain boundary mobility is not related to temperature by Eqn. 2. This equation introduces a time-dependent exponent, m, while keeping grain growth exponent in Burke's equation¹²²:

$$D^2 - D_0^2 = 2Kt^m (8)$$

The time-dependent exponent accommodates factors which slow grain boundary mobility, such as grain boundary pinning or solute drag.

The above mentioned grain growth models predict unlimited grain growth. However, due to geometrical factors and energy considerations, as well as sample thickness, at extended time grain size may reach a maximum. The modified Kolmogorov–Johnson–Mehl–Avrami (KJMA) is normally used for accurate fitting of specific types of phase transformation:

$$\frac{R_t^3}{R_{max}^3} = \frac{R_o^3}{R_{max}^3} + \left(1 - \frac{R_o^3}{R_{max}^3}\right) \left[1 - \exp(-Kt^{\alpha})\right] \quad (9)$$

where R_t is grain size at time t, R_o is initial grain size, and R_{max} is limiting grain size. However, it has been successfully applied to systems with limited growth exhibiting sigmoidal trends. Although the rate constant and Avrami exponent are not directly comparable to the rate constant and growth exponent of the classical parabolic model, maximum grain size and behavior can be predicted.

Chapter 4.3 Proposed Mechanisms for Coarsening

Ceria based inverse opals are shown to exhibit similar grain growth behavior to inverse opals made of metals and other oxides. Materials templated to have structures with large pores are known to have limited diffusion across macropores¹⁰³. Specifically, inverse opal structures tend to behave uniquely at high temperatures. Previously, authors have shown that grains in dense areas of inverse opals (at the center of the node or strut) grow faster and also grow to be larger

than in sparsely populated areas (near the surface)¹²³. In this work, authors perform *in situ* high temperature TEM (HT TEM), and observe this phenomenon for cobalt metal, nickel oxide and iron oxide, as shown in Figure 31.



Figure 31: Bright-field TEM images from in situ heating of iron oxide inverse opals at (a) and (b), 19°C; (c–k), 650°C, 9–45 min; (l) and (m), 750°C, 47 min; and (n–q), 950°C, 98–128 min¹²³.

Coarsening is characterized by a decrease in the number of grains per unit volume over time. Two of the resulting outcomes of coarsening are 1) growth of large grains while small grains shrink, or 2) coalescence. Qualitatively, coarsening appears to be occurring within inverse opals subjected to annealing, as seen in Figure 32. The characteristic mechanisms behind diffusion controlled late-stage coarsening can be elusive. However, isothermal grain size as a function of time, particle size distribution, grain boundary energy and activation energy can give clues to underlying phenomena. In an attempt to understand the fundamental mid-stage coarsening mechanisms occurring as a result of the continuous porosity within inverse opals, TEM heat treatment studies were conducted.



Figure 32: In situ SEM of 300nm ZDC20 inverse opal heated to 950°C, 1050°C, and 1150°C.

Ostwald ripening does not appear to be the dominant mechanism of diffusion within the ceria inverse opal grain structure. Vapor-phase transport is too low for Ostwald ripening to occur in ceria-based materials at the temperatures mentioned in this work. Since the melting temperature of zirconia doped ceria is high (~2400°C for ZDC20 according to the CeO₂-ZrO₂ phase diagram), and its vaporization temperature even higher, it is fair to assume that the vapor pressure of cerium

oxide is low^{29} . In addition, the vapor pressure of cerium oxide is expected to be lower than that of pure ceria, which is $\sim 5 \times 10^{-10}$ atm at 1100°C, according to the PV expansion equation:

$$\log(p) = A + \frac{B}{T} + C * \log(T) + \frac{D}{T^3}$$
(10)

where p is in atmospheres, and for pure ceria A=5.611, B=-21200, and C,D=0¹²⁴. Moreover, the initial stage grain growth is very rapid, so the Gibbs-Thomson effect is not likely contributing to the vapor pressure at the time scales required for thermochemical cycling. Inverse opals can be considered highly porous structures where pore diameter is much larger than grain diameter and cross-pore distances are large. For these reasons, Ostwald ripening is not likely the dominant mechanism. Instead, for the present work, coarsening can be controlled by neck growth in porous domains and curvature driven boundary migration in dense domains¹⁰⁶.

According to Blanford *et al*¹²³, at high temperatures, grains within denser parts of inverse opals (nodes) will grow faster than those at the edges (struts). This is a clue as to why grain growth occurs faster at the node than the strut. Additionally, pore window diameter increases as the small grains at the window's edges are consumed to grow larger inner grains, which exist in more densely populated areas. Apparently, if grain growth is dictated by temperature, and not by time, it is a diffusion limited process, and is not limited by addition of atoms to the interface.

We hypothesize that the grain growth within the node of the inverse opal occurs faster than in the struts. Although, coarsening is dominated by surface diffusion within both the node and the struts (Figure 33), this hypothesis is based on the recognition that more grains within the struts are adjacent to pores, so that the grain/pore boundary ratio is much higher in struts than in nodes.







Figure 33: a) Proposed coarsening model where material diffuses from strut to node b) qualitative observation of coarsening using *ex situ* TEM bright field imaging of ZDC20, 1µm inverse opals.

Qualitatively, this model is validated through TEM images of ZDC20 inverse opals annealed at 1100°C for extended time. The starting materials have fine grains in both the node and strut, but over time, the grains at both strut and node grow and reach a critical size. This is where the diameter of the node/strut is equal to the grain size. As this occurs, the material becomes susceptible to thermal and mechanical shock, as well as thinning of the struts, and breakage is evident. After breakage, if the material is allowed to undergo further annealing, it will eventually distort and ordered porosity will be lost.

Chapter 4.4 Experimental

As-prepared samples (Chapter 2) were exposed to high temperatures for the purpose of grain growth observation. ZSC20 1µm inverse opals were placed in high form alumina crucibles and subjected to heating at 900°C, 1000°C, and 1100°C for up to 72 hours in air. Samples were removed at different time points to observe grain growth and structural changes as a function of time. The control powder was subjected to heating at 1100°C for various time in air. Upon removal from the furnace, all samples were air-quenched in order to halt thermal changes.

Chapter 4.4.1 Ex Situ Grain Size Measurements

Ex situ transmission electron microscopy (TEM) was used to characterize grains within inverse opals and control powders. Sample preparation deviated from tradition TEM methods due to the small amount of powder available. TEM samples were prepared by placing a small amount of ceria/zirconia powder onto a disposable glass slide, applying a single drop of ethanol on top of the powder, and hand-crushing the powder using a clean tweezer. A lacey carbon on Formvar coated 200 mesh copper grid was then dragged through the dilute ceria/ethanol slurry. Once dried, the samples were imaged using the FEI T12 120kV TEM or FEI Titan STEM 300kV TEM (for asprepared samples having grain diameter <10 nm), located at the Electron Imaging Center for Nanomachines (EICN), within UCLA's California NanoSystems Institute (CNSI). High contrast bright-field images were obtained by using an objective aperture to block the diffracted beam within the TEM, leaving the transmitted beam only for imaging (Figure 34(a)). In addition, to verify the single-crystalline nature of the grains, dark-field imaging was used. Here, the beam is

shifted so that the transmitted beam is blocked, and only certain diffracted beams pass through the aperture, making up the image (Figure 34 (b)) Representative bright-field and dark-field images of ZSC20 inverse opals are shown in Figure 35.



Figure 34: Simplified beam-path schematic in TEM when imaging in a) bright-field settings and b) dark field settings.

Grain sizes were measured using the open source software, Fiji Image J. First, the scale of each image is set by drawing a line over the scale bar and defining the pixel to nm ratio. Next, lines are drawn along the longest diameter of the grain, in the case where they are no longer spherical in shape. At least 100 grains were measured for each ZSC20 sample after heat treatment.



Figure 35: Representative TEM images of as-prepared ZSC20 1 micron inverse opal a) dark-field image, b) bright-field image.

Chapter 4.4.2 In Situ SEM Heating Experiments

In situ SEM heating was performed to monitor changes in macroscopic features. For this purpose, the Protochips Aduro 500 heating stage was used. The sample area is heated by resistive heating of a substrate chip. The substrate chip, named the "E-chip" has small area coated in a proprietary oxide, as shown in the inset of Figure 36. The oxide has copper leads integrated into the chip, which are connected to the heating platform during use. To prepare samples for heating, a small amount of powder sample is dispersed in a 0.10 mL drop of isopropanol. The dispersed powder is dropped onto the substrate chip and allowed to dry. Next, the chip is connected both mechanically and electrically to the heating stage using small copper teeth, as shown in Figure 46. At this point, the stage with the E-chip is inserted into the SEM (FEI Nova Nano), and connected to the external power source via copper wire.



Figure 36: Aduro heating stage and sample preparation platform, with copper "teeth" shown in dashed lines. Inset of E-chip setup.

High-quality SEM images of inverse opals were obtained throughout the heating experiments. Although the ceria/zirconia inverse opals were insulating, and subject to surface charging, short dwell times allowed the use of high vacuum mode without any additional sample preparation. The chamber was kept at 10⁻² Pa, and an immersion lens was used to obtain optimal focus at high magnification (100kX). Images were taken using a 50 ns dwell time, integrated over 16x.

Isothermal heating experiments at 1100°C allowed recording of *in situ* structural changes for up to 15 hours. Once an optimal sample area was found, it was heated from 0-1100°C at a rate of 200°C/minute, to minimize thermal drift during heating, ensuring that the sample viewing area was always visible. Instead of low-quality video capture, higher-quality images were taken at prescribed time intervals. For the first 10 minutes, an image was captured every minute. Over

longer times, image capture was less frequent, as any thermal changes were expected to be exponential in nature. After the experiment was finished, and the last image acquired, the E-chip is quickly cooled to room temperature. Upon rapid cooling, the oxide film burst, making the E-chips single-use.

Image J was used to measure the feature sizes of the images taken during *in situ* experiments, including strut thickness, window diameter, and relative areal density.

To solve for an empirical formula relating microscopic and macroscopic feature growth, scaling factors were found at each data point in time. The window diameter was divided by the grain size, and the resulting data was fitted to a hyperbolic decline:

$$\frac{W_D}{D} = q_o * (1 + \frac{bt}{a})^{-1/b}$$

where W_D is window diameter, and D is grain size. Using CurveExpert Pro, W_D/D is plotted vs. time, and the empirical parameters are fitted in the software using least-squares methods.

Chapter 4.5 Grain Growth Studies

ZSC20 inverse opals were annealed at 900, 1000, and 1100°C for up to 72 hours. These materials were placed in a preheated furnace, and air quenched upon removal. Grain growth was monitored through *ex situ* TEM.

ZSC20 inverse opal grain size after annealing was compared to that of the powder control in Figure 37. Initially, growth is faster in the inverse opal than in the powder control, as inverse opal grains are close-packed, while the grains within the powder control are loosely packed. Intimate contact between grains allows for more diffusional pathways, and for faster diffusion to occur. Over time, the grains of the powder control grow to be larger than those of the inverse opal. As the grains within the inverse opal grow to sizes on the same order of magnitude as the node and strut thicknesses, the number of nearest-neighbors decreases, and diffusion is limited to the surface. Conversely, over time at high temperatures the grains in the powder control densify, and intimate contact is further increased. Grain size in the powder control is not limited by macrostructure, but grain size in the inverse opal is severely limited by interconnected porosity.



Figure 37: Grain growth as a function of time for ZSC20 1µm inverse opal and powder control annealed at 1100°C.

ZSC20 grain growth rate is dependent on annealing temperature. Figure 36 plots grain size vs. time for annealing at 900°C, 1000°C, and 1100°. As expected, grain growth rate increases

drastically with temperature. At 900°C and 1000°C, grain diameter appears to approach a maximum value, although at 1100°C, this phenomenon is not immediately clear in Figure 38.



Figure 38: Grain size of ZSC20 inverse opals annealed at 900°C, 1000°C, and 1100°C.

Although linear plots are helpful qualitatively, no useful parameters can be extracted without modeling these data. In order to obtain a first guess of grain growth exponent, grain growth data is plotted logarithmically in Figure 39.



Figure 39: Logarithmic plot of lnD vs. lnt for ZSC20 inverse opals annealed at 900°C, 1000°C, and 1100°C

Table 6: Grain growth exponents and rate constants derived from lnD vs. Int for ZSC20 inverse opals.

Annealing T (°C)	K _{strut} (nm/hr)	n _{strut}
900	12	9.1
1000	16	5.0
1100	56	2.8

From the linear plots of lnD vs. lnt, grain growth exponents can be found from the slope of the curves, and rate constant can be found from the y-intercept. At low temperature (900°C), the grain growth exponent is 9.1, which is near the value known for grain boundary relaxation in nanocrystalline materials¹²⁰. Grains within ZSC inverse opals are <10nm as-prepared, and nanocrystalline materials have many high-angle, high energy grain boundaries. At this temperature, some high energy processes such as grain boundary diffusion and lattice diffusion, might not be activated. Instead, bending and stretching of Ce-O bonds across the interface of the grain boundary may be occuring as grains grow, which does not require material diffusion. This relaxation lowers the overall energy of the system by decreasing the grain boundary angles. At 1000°C, the grain growth exponent is 5, which approaches a more classical value. At this intermediate temperature, grain growth is still relatively slow, as the rate constant of 16 is only slightly larger than that of the rate constant at 900°C (12). In addition, grain boundary relaxation is no longer a dominant growth mechanism, and diffusion processes are activated. At 1100°C, the grain growth exponent is 2.8, which is in between the "normal" exponent value of 2, and the Ostwald ripening value of 3. The rate constant is nearly 5 times larger than that of growth at 900°C. At 1000°C and 1100°C, grain growth is diffusion limited.

In order to gain insight on the type of diffusion at occuring during grain growth of ZSC20 inverse opals, the activation energy for the diffusion process must be obtained. An Arrhenius plot of lnK vs. 1/T is shown in Figure 40.



Figure 40: Arrhenius plot of lnK vs. 1/T for ZSC inverse opals annealed at 900, 1000, and 1100°C.

The activation energy is related to K and T by the following equations:

$$K = K_o \exp\left(\frac{-Q}{RT}\right) \quad (11)$$
$$lnK = lnK_o - \frac{Q}{R} \cdot \frac{1}{T} \quad (12)$$

The activation energy was found to be ~ 103 kJ/mol, which is low compared to the typical values for grain boundary diffusion of ceria, which can be as high as 600 kJ/mol^{99} . Normally the

activation energy of lattice diffusion is larger than grain boundary diffusion, which is greater than surface diffusion:

$$Q_{lattice} > Q_{GB} > Q_{surf}$$
 (13)

Typical activation energy for surface diffusion of ceria is ~110 kJ/mol¹²⁵. From these data, the dominant grain growth mechanism is by surface diffusion.

Although surface diffusion has been found to be dominant, prediction of growth behavior and full understanding of growth phenomena requires a quantitative description of grain growth. Figure 41 plots grain growth data for ZSC20 inverse opals annealed at 1100°C. These data are fit to Burke, Höfler and Averback, and KJMA models (Eqs. 7, 8, 9). The best fit is achieved with the KJMA model, which assumes a maximum grain size of 300nm. The coefficients of determination (r² for non-linear fit) for Burke, Höfler and Averback, and KJMA model achieves the best fit. This implies that there are factors affecting grain growth as to fully stop growth progression over time.

Figure 42 plots ZSC20 non-templated control powder annealed at 1100°C. When fit with Eqs. 7, 8, 9, the coefficients of determination are 0.97, 0.99, and 0.96 for Burke, Höfler and Averback and KJMA models, respectively. Here, the best fit is obtained using the Höfler and Averback equation, implying that there is no maximum grain size hindering grain growth. Additionally, growth is parabolic, and factors that change diffusion parameters in the inverse opal may not be present in the powder control, such as macroporosity. This result agrees with the hypothesis that the porosity in inverse opals hinders grain growth, and maximum grain size is reached with the

strut thickness is equal to the grain diameter, as maximum grain size using the KJMA equation is set to 300nm.



Figure 41: Fit of ZSC20 1µm inverse opal grain growth data to Burke, Höfler and Averback, and KJMA equations. Best fit is obtained using KJMA equation with 300nm maximum grain size.



Figure 42: Fit of ZSC20 powder control grain growth data to Burke, Höfler and Averback, and KJMA equations. Best fit is obtained using Höfler and Averback's equation.

Secondary phases and porosity may interrupt grain growth by lowering the driving force for grain boundary migration, even in materials with low Zr content. ZSC20 has been previously established as a benchmark material. This Zr addition allows for improved thermal stability over pure ceria without the tetragonal phase being formed. In a solvent matrix that has a dispersed secondary phases, there is a restraining force P that acts upon the grain boundary:

$$P = \frac{3f\gamma}{2r} \qquad (14)$$

where f is the volume fraction of particles with radius r. This force effectively impedes the motion of the grain boundary, eventually halting grain growth entirely. The resulting maximum grain size is given by

$$D_{max} = \frac{4r}{3f} \quad (15)$$

where this effect is termed solute $drag^{126}$.

In situ X-ray diffraction measurements indicate some secondary tetragonal phase formation in as-prepared, and annealed ZSC20 powders (Ch. 2). Additionally, small pores (2-5 nm) are present in TEM images of ZSC20 materials in both as-prepared and annealed at 1000°C for various times, as shown in Figure 43. This is indicated by small grains having lighter areas (pores) of TEM diffraction contrast.



Figure 43: Bright-field TEM images of ZSC20 a) inverse opal annealed for 1 hour, b) powder control annealed for 1 hour, and c) powder control annealed for 4 hours at 1000°C. Arrows point to lighter areas indicating porosity.

Fitting grain growth data to the limiting grain size KJMA model can verify that macroporosity limits the grain size in inverse opals, as opposed to secondary tetragonal phases or microporosity that may be present in some of the materials. Figure 44 plots the fit of the KJMA equation to grain growth data for ZSC20 powder control with R_{max} =300, 3,000, and 30,000 nm. The coefficient of determination for R_{max} =3,000nm is the same as that for R_{max} =30,000 nm (0.99), both of which are better fits than 300 nm (0.96). This points towards unlimited grain growth in ZSC powder controls, uninhibited by ordered porosity. For ZSC20 inverse opal materials, the secondary phases arising from local inhomogeneities and micropores are not at cause for slowed grain growth. Instead, we can attribute the slower rate to be the result of macroporosity.



Figure 44: Grain growth data of ZSC20 powder control annealed at 1100°C fitted to KJMA model with maximum grain radius of 300nm, 3,000nm, and 30,000nm.

Chapter 4.6 Relating Microscopic and Macroscopic Behavior

In situ SEM was used to monitor macroscopic changes during high temperature annealing of ZSC20 1µm inverse opals. Structural changes, such as strut thinning and breakage, as well as window diameter changes, can be obtained from the qualitative image observation of Figure 45. In Figure 45(a), grains of the pristine, as-prepared inverse opal can be seen. Small, loosely packed grains can be seen on the surface of the inverse opals, similar what is seen previously in Figure 45 (b). Small grains can also be seen in high resolution ex situ SEM images of pristine material, shown in Figure 46. In addition, the struts are thick and robust, although there is some inherent inhomogeneity in the strut thickness. As the pristine structure is exposed to annealing at 1100°C under vacuum (Figure 45), the most obvious change is the smoothing of the walls of the inverse opals (Figure 45 c). After only 10 minutes at 1100°C, some of the small grains at the wall edges are no longer visible (Figure 46 c), and after 2 hours the walls are completely smooth (Figure 45 d). These results corroborate the explanation of steep change in gamma in Chapter 3 (Figure 23 a), after 1 hour at 1100°C. Coarsening and surface area loss at temperatures higher than 800°C, is evident both in situ (Figure 45) and ex situ (Figure 33). Strut thinning appears to occur in areas of inhomogeneity, where the strut is thinnest. After 6 hours, the first strut break can be seen, as indicated by the arrow in Figure 45(g), and the gap grows as time passes. After 15 hours (Figure 45 i), many of the struts are broken, and many of those that are intact are thinning. A gradual loss of order is expected, from the analysis in Chapter 3, but here it can be seen in situ with increasing strut breakage. Interestingly, small grains in the background appear to coarsen, as indicated by dashed circles in Figure 45 (c), (f), and (i), and the pores between them increase in size.


Figure 45: *In situ* SEM images of ZSC20 1µm inverse opals a) before annealing, and annealed at 1100°C for b) 10 minutes, c) 1 hour, d) 2 hours, e) 3 hours, f) 4 hours, g) 6 hours, h)11 hours, and i) 15 hours and 15 minutes. Arrows indicate broken struts, dashed circles highlight background grain growth.



Figure 46: High-resolution SEM images of pristine ZSC20 inverse opal showing a) macrostructure, and b) microstructure. Individual grains are clearly visible.

In situ experiments mimic operational conditions. Initially, it was expected that the structural break-down would be accelerated during *in situ* experiments due to faster diffusion caused by an increased number of oxygen vacancies. However, this does not appear to be the case, as breakage occurs after annealing for some time between 1 to 6 hours. This result is consistent with the FFT analysis presented in Chapter 3. The material behavior during *in situ* experiments resembles those

during *ex situ* heating experiments done in ambient atmospheres. Thus, *in situ* heating can be used to accurately assess inverse opal stability during operation.

Quantitative measurements were made using *in situ* SEM. Figure 48 plots the decrease in strut thickness over time, alongside the increase in window diameter over time. In Figure 47 (a), the window diameter increases rapidly at short times, followed by a steady increase. Concurrently, the strut (wall) thickness initially decreases rapidly, followed by a slight, steady decrease for the first 4 hours. After 6 hours, the strut thickness decreases sharply, due to the beginning of strut breakage. This discontinuity makes the transition from an ordered structure to a disordered structure (as described in Chapter 3), obvious. In addition, the increase in window size indicates structural coarsening, further supporting the original hypothesis of failure by coarsening. Figure 47 (b) plots the grain growth data obtained from *ex situ* TEM heating studies alongside *in situ* SEM window diameter measurements. Both of these feature sizes appear to increase logarithmically, and qualitatively appear to be scalable.



Figure 47: Quantitative *in situ* SEM analysis comparing a) wall (strut) thickness and window diameter, and b) grain size and window diameter.

Material features such as grain size, density, or pore fraction, which span orders of magnitude, are related. Herring first proposed scalability between grain size and density in porous compacts, allowing for prediction of the degree of densification at a particular time, given a second porous compact with known sinterability¹²⁷.

By understanding the scalability of microscopic and macroscopic features of one system, Herring's laws of scalability allow prediction of growth behavior of a similar system. By observing large, macrostructural changes, we can have an idea of grain structure (and vice-versa). Here, the empirical relationship between inverse opal window diameter and grain size was found to be:

$$W_d = D * 34.6 * (1 + \frac{2.3t}{0.05})^{-\frac{1}{2.3}}$$
 (16)

where this relationship was found using methods described in Chapter 4.3.2. This equation can be used to predict feature size in ZSC20 inverse opals at 1100°C, if an annealing schedule is known. Table 7 summarizes data obtained by application of the empirical relationship to *ex situ* window diameter measurements. Although the error is high for 0 and 1 hour, the trend of grain growth is preserved.

Time (hours)	Measured window diameter (nm)	Predicted grain size (nm)	Actual grain size (nm)	% Error
0	259	7	11	34
1	305	47	30	59
6	318	106	102	4

Table 7: Window diameter and grain size of ZSC20 1μm inverse opals from *ex situ* TEM heating at 1100°C, and calculated grain size from empirical relationship

Chapter 4.7 Conclusion

The microstructure of ZSC20 materials was studied as a function of high temperature annealing. TEM grain size measurements shed light on the mechanisms behind inverse opal high temperature degradation. From these analyses, the dominant mechanism of coarsening in ZSC20 inverse opals was found to be by surface diffusion.

Inverse opal macroporosity has a measurable effect on high temperature behavior. Grain growth was hindered by macroporosity in inverse opals, but unaffected in powder controls. This analysis corroborates our hypothesis that grain growth differs in materials with continuous porosity from bulk materials. Finally, an equation governing the scalability of inverse opal grain size and window thickness was generated. Using this equation, future macroscopic behavior and lifetime limits can be predicted.

Chapter 5 Isothermal Chemical Cycling of Inverse Opals

Chapter 5.1 Motivation

In order to verify the benefit of ordered porosity for thermochemical fuel production, it is necessary to subject these structures to thermochemical cycling. Thus far, isothermal cycling has been performed by our collaborators in Sossina Haile's group at Caltech. These cycles include a reduction step by with H₂, followed by an argon purge to rid the system of hydrogen, and an oxidation step using superheated steam.

Previously, ceria based inverse opals have been compared to materials with random porosity for their ability to produce solar fuels. Carbon monoxide, hydrogen, and syngas, a 1:2 mixture of the two, have been produced efficiently using these materials^{90,128}

Isothermal chemical cycling is a useful tool for evaluation of hydrogen productivity of inverse opals. This type of reaction protocol mitigates the effects of heat loss associated with large temperature swings, as well as coarsening effects associated with high temperatures. The purpose of these experiments is to quantitatively compare the hydrogen production rate of non-templated ceria-based materials to ZSC inverse opals having different pore sizes.

Chapter 5.2 Experimental

Inverse opal macrostructures were isothermally cycled at 800°C in different gas environments along with randomly porous powders to evaluate the effect of periodic structure on hydrogen production efficacy. ZSC20 inverse opals having 300nm, 650nm and 1µm nominal pore sizes, and powder control were subjected to isothermal treatment under a chemically cycled gas. First, 0.5g ceria material was heated at a 10 degree/minute ramp rate in air to 800°C in an infrared furnace. The furnace contained a quartz tube ~1cm in diameter in which the samples were packed. Glass

wool was packed in the quartz tube both upstream and downstream of the test samples, as shown in Figure 48.



Figure 48: Isothermal chemical cycling setup.

The quartz tube inlet is connected to several flanges upstream. These flanges connect to a hydrogen source (H₂ in Ar gas cylinder), and a system which bubbles air through H₂O to create wet air. The gas from the quartz tube is analyzed by a thermal gravimetric mass spectrometer. After heating the horizontal fixed bed to 800°C, the samples are purged with Ar gas, and the cycling was initiated. During the first experiment, with 300nm, 650nm, and μ m inverse opals, samples were reduced for 20 minutes using 2.95% H₂ in Ar at a flow rate of 200 sccm, followed by a 5 minute Ar purge. Subsequent experiments used a reduction time of 30 minutes. Next, oxidation occurred using a wet Ar stream (35% H₂O, 638 sccm), followed by a 5 minute Ar purge at 1000 sccm. At the end of 12 cycles, a 2 hour gas calibration was performed, for a total dwell time at 800°C of approximately 12 hours. As a control, samples having the same inverse opal morphologies and

pore sizes as those treated under chemically cycled gas were heated to 800°C under a fixed gas (air) for 12 hours.

Chapter 5.3 Comparison of Ce_{0.6}Zr_{0.4}O₂ Materials

Hydrogen production rate for ZSC40 inverse opals and powder control is shown in Figure 49. Results in Figure 49(a) indicate an increase in hydrogen production rate in ZSC40 inverse opals having 1µm pore size, over that of non-templated control powder. The Ar purge time in between cycles (for removal of hydrogen) in the Figure 49(a) is 45 min while the purge time in the Figure 49(b) is 5 minutes. Unfortunately, due to the change in cycling temperature and reactor conditions, these results are not directly comparable. Subsequent tests are performed at 800°C. In Figure 49(b), the hydrogen production rate increase is slight upon increasing water vapor pressure from 0.03 to 0.15 atm. This could be attributed to surface reaction limitations at high flow rates, as opposed to mass transport limitations, as described in Chapter 1 (Figure 5). A difference in the performance of inverse opal and non-templated powder can only be seen under mass transport limited conditions, as surface reaction kinetics are the same for materials of identical composition.



Figure 49: Isothermal hydrogen production experiments of ZSC40 (a) 1µm inverse opal and powder control at 800°C, (b) 1µm inverse opal at 650°C.

Chapter 5.4 Comparison of Ce_{0.8}Zr_{0.2}O₂ Materials

Figure 50 plots isothermal hydrogen production for non-templated control powder, 300nm pore-size inverse opal, 650nm pore-size inverse opal, and 1µm pore size inverse opal. These experiments were performed using the same experimental parameters described previously in section 5.2. From these data, we see similar kinetics for all samples. However, as summarized in Table 8, the 1µm inverse opal yielded the largest total amount of hydrogen (7.3 mL/g), which was cumulatively during the experiment. From the calculations performed in Chapter 2, we would expect to see an increase in hydrogen production with increasing pore size, and furthermore, we also would expect to see increased hydrogen production of inverse opals over non-templated material. The overall amount of hydrogen produced was noticeably greater for 1µm inverse opals, while all other samples behaved similarly. These results do not match those of previous works,^{88,129} where reduction time is shorter than in the experiments reported here. Also, the reduction stream has a lower percentage of hydrogen than some of the experiments reported in literature.



Figure 50: Isothermal hydrogen production rate data at 800°C for ZSC20 a) powder control, b) 300nm inverse opal, c) 650nm inverse opal, and d) 1000nm inverse opal.

Table 8: Maximum hydrogen production rate and amount from isothermal thermochemical

 cycling done using ZDC20 inverse opals (Caltech)

Material	Max. H ₂ Production Rate (mL/min/g)	Amount H ₂ Produced (mL/g)
Control	4.0	5.8
300nm	3.7	6.0
650nm	3.7	5.7
1000nm	3.9	7.3

The similarity in kinetics between the 1µm inverse opal and powder control are most likely due to a surface-reaction limited oxidation process. This phenomenon can be explained by recent

literature on the effect of flow rate during the oxidation step, as explained in Chapter 1. The flow rate used here is >1278 mL/min/g, as 638 sccm is used with 0.5g of material, and the flux of gas molecules at STP is greater than at high temperatures due to density effects. This is much greater than the previously established maximum flowrate of 300 mL/min/g. Although the density of carbon dioxide differs slightly from that of water vapor, assuming they are the same gives a rough approximation applicable to the system presented here. At this flow rate, the oxidation reaction is most likely surface reaction limited, and hydrogen production rate depends solely on material, not macrostructure. At flow rates less than 300 mL/min/g, the system is mass transport limited, and there is no need for excess heat recovery for unused gases. This explains the similarity in hydrogen production rate of inverse opals and non-templated materials.

In Chapter 2, the potential for use of ZSC20 inverse opals at higher temperatures was established. In addition to gamma, surface area measurements of inverse opals before and after thermochemical cycling can point towards structural collapse. Figure 51 plots BET surface area of a) ZSC20 and b) ZSC40 inverse opals before and after isothermal cycling at 800°C. Here, surface area before and after thermal cycling at 800°C is of the same order of magnitude. This further corroborates the previously established hypothesis that these materials can be cycled at temperatures higher than 800°C without structural collapse.



Figure 51: Specific surface area from BET nitrogen sorption measurements of a) ZSC20 powder control, 300nm inverse opal, 650nm inverse opal, and 1µm inverse opal, and b) ZSC40 powder control and 1µm inverse opal before and after isothermal chemical cycling at 800°C.

A comparison of hydrogen production from inverse opals having pores spanning an order of magnitude is shown in Figure 52. Here, the 1 μ m inverse opal clearly outperforms the powder control, 300nm inverse opal, and 4.3 μ m inverse opal. This result is unexpected based on the estimate of fluid flow through pore windows. We expect to see an improvement in hydrogen production kinetics for inverse opals with pore sizes >1 μ m, and higher hydrogen production rates for inverse opals of all sizes when compared to non-templated materials.

The addition of graphene to polystyrene beads used in the large pore (>1 μ m) inverse opal synthesis may affect its redox properties. Although 800°C is usually an adequate temperature for carbon removal, some authors suggest that higher temperatures or long dwell time at 800°C may be needed to remove residual graphene^{130,131}. The low cumulative hydrogen production (Table 9) is most likely attributed to this carbon impurity. In addition, visual inspection of large-pore inverse opals after mechanical agitation indicates breakage and settling of the material, which may be more mechanically unstable than their sub-micron pore counterparts. Both of these factors may be contributing to the low hydrogen production rate for 4.3 μ m inverse opals.

Flow rates used during the oxidation step may also affect cycling conditions. As mentioned previously, a maximum flow rate of 300 mL/min/g should be used in order to observe improvements with changes in macrostructure. Similar to other experiments described here, the flow rate during the oxidation step is much greater than 300mL/min/g, which is most likely masking any effect of porosity.



Figure 52: Figure 50: Isothermal hydrogen production rate data at 800°C for ZSC20 a) powder control, b) 300nm inverse opal, c) 1000nm inverse opal, and d) 4300nm inverse opal.

The difference in cumulative amount of hydrogen produced between architectures is obvious in this experiment, as summarized in Table 9. Again, 1µm inverse opals yield the maximum amount of hydrogen, 7.76mL. These results agree with the results of the previous experiment; however, due to the effect of high flow rate on transport regime, the true influence of ordered porosity on hydrogen production cannot be seen.

	Max. H2 Production Rate	Amount H2 Produced	
Material	(mL/min/g)	(mL/g)	
Control	3.7	6.3	
300nm	3.0	6.3	
1000nm	4.6	7.8	
4300nm	3.2	4.3	

Table 9: Results of maximum hydrogen production rate and amount from isothermal

 thermochemical cycling done using ZDC20 inverse opals (Caltech).

Chapter 5.5 Conclusion

Inverse opals were evaluated for their hydrogen production capability compared to that of nontemplated control materials. Surprisingly, in all cases for ZSC20 inverse opals, a kinetic improvement is not apparent, yet cumulative hydrogen production reaches a maximum for 1 micron inverse opals. The expectation is that flow rates for this experiment need to be lowered in order to observe reactions in the mass transport limited regime. Although puzzling, these results point to a need for testing at higher temperatures; we previously established that these materials are robust up to 1000°C.

Chapter 6 Conclusions

Ceria-zirconia inverse opals have the potential for thermochemical hydrogen production at temperatures upwards of 1000°C. Previously established temperature limits for these materials hinder the hydrogen production capacity, concealing the kinetic advantage of inverse opal macrostructures. Here, a method of quantification of inverse opal thermal stability has been established, and an ideal zirconia content for achieving thermal stability without the formation of undesirable tetragonal phases has been found. In addition, this robust method can be applied to other systems having ordered porosity, allowing for prognostic information on the lifetime of materials used for high temperature applications, especially thermochemical fuel production.

Insights on degradation mechanisms of inverse opals during high temperature applications are presented in this dissertation. Inverse opals are unique when compared to materials of similar composition due to their macroporosity, which was found to inhibit grain growth in these materials. Furthermore, macroscopic feature changes in these materials are directly scalable to microscopic feature changes. This knowledge allows for prediction of grain structure at the nano-scale, when observation is only possible on the micro-scale. The impact of this known scalability is an ease of characterization during real-world operation.

Finally, inverse opal pore structure does have an effect on hydrogen production capability. ZSC20 inverse opals having 1 micron pore size remain the best material in terms of overall hydrogen production capacity, but there appears to be no improvement in the production rate. These results are unexpected, and most likely due to high gas flow-rates, where the rate of hydrogen production is governed by surface reaction kinetics, and not mass transport. This work presents an opportunity for further research into materials with ordered porosity for thermochemical hydrogen production, in order to harness the full kinetic benefit of inverse opal architectures.

Appendix A: Motivation for Increasing Template Bead Size

The motivation for increasing inverse opal pore size is improvement in mass transport by increasing diffusivity. Active materials within thermochemical reactors can be modeled as packed beds in fluidized bed reactors⁴³. In these systems, the radii of small pores present in high surface area active materials dictate the flow regime of fluid flowing over the material. Within the molecular flow regime, the mean free path of the fluid is much less than the diameter of the pore, and particle-particle interactions dominate flow. In contrast, within the Knudsen flow regime the mean free path of the gas is greater than the pore diameter, and particle-pore wall interactions dominate, as illustrated in Figure A1. For gases, typical diffusion coefficients within the molecular regime and Knudsen regime are 10⁻¹, and 10⁻⁵ to 10⁻², respectively^{132,133}.



Figure A1: a) molecular flow: the mean free path of the gas is much smaller than the characteristic length, and b) Knudsen flow: the mean free path of the gas is greater than the characteristic length of the vessel.

To determine the diffusion regime within the pores it is useful to compare the mean free path of the gas molecule to the pore diameter, which results in Knudsen number¹³⁴:

$$Kn\# = \frac{\lambda}{d} = \frac{k_B T}{\sqrt{2}\pi\sigma^2 pd} \qquad (1)$$

where d is the pore diameter, λ is the mean free path, k_B is the Boltzmann constant, T is the temperature, σ is the hard sphere diameter of a gas molecule, and p is the pressure. When Knudsen number is much smaller than unity, molecular flow is dominant.

The hard sphere radius can be estimated using the second coefficient of the virial expansion, which simplifies to the second parameter of the Van der Waals equation of state. This parameter, the Van der Waals volume, takes into account the volume exclusion of gas molecules¹³⁵. For a rough approximation, the hard sphere radius is determined from the Van der Waals volume of the gas using the relation:

$$b = Na * \frac{4}{3}\pi \left(\frac{\sigma}{2}\right)^3 \qquad (2)$$

Where b is the Van der Waals volume $[m^3/mol]$ and Na is Avogadro's number.

To estimate the minimum pore radius which ensures flow within the molecular regime, Knudsen number is set to 0.5 at atmospheric pressure, and pore window diameter can be solved for. From visual inspection of inverse opal pores, the window diameter is approximately 1/3 to 1/2 of the pore diameter (Figure A2), and 1/3 is used as a conservative estimate.

Table A1summarizes the minimum pore diameters for the gases in this system. A minimum pore diameter of \sim 4.5µm should guarantee molecular flow.



Figure A2: SEM image of 4.3µm inverse opal showing pore window.

Table A1: Estimated minimum pore diameters for flow within the molecular flow regime¹³⁵.

Gas	b/10 ⁻⁵	Min. Pore Diameter (µm)	
Uas	(m ³ /mol)	800°C	
Water	3.1	4.2	
Oxygen	3.2	4.2	
Hydrogen	2.7	4.8	

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