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Title: "In Situ Characterization of the Nanoscale Catalysis during Anodic Redox Process"

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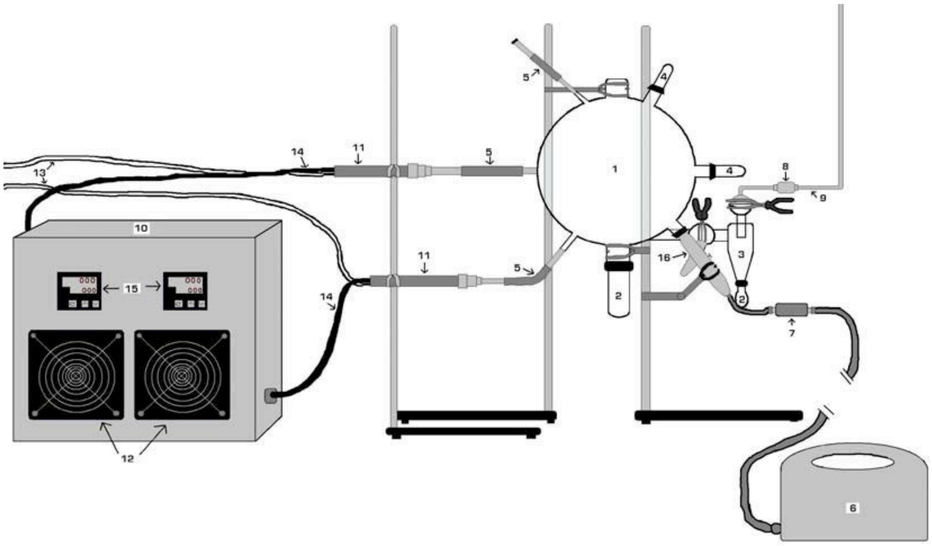
Accomplishments:

1. Building a Spray Drying System and synthesis of high surface area Ceria and Pr-doped ceria

We have used direct calcination and spray-drying methods to synthesize ceria and doped ceria high surface area samples. For spray drying, we have designed and built a system to synthesize mixed oxides and cermets (Figure1). This technique has provided better control on the homogeneity and the size of nano particles. The spray drying system consists of a glass vessel, with several alternative inlet positions for salt solution sprayer, inlet for hot air at controlled temperature and pressure, and removable sample collector (Figure 1). The idea is to spray the mixed solution of salts in to the glass vessel under flow of hot air (above or near the decomposition temperature of the salts). Powder thus collected was further calcined in air at 500 °C, 700 °C and 900 °C for 2, 4 and 6 hours. After



Spray Drying System Key

1. Spray drying chamber
2. Sample collection container
3. Vortex
4. End caps for alternate air brush ports
5. Heat gun ports
6. Air compressor
7. Moisture trap
8. Exhaust filter
9. Exhaust line
10. Electrical component box
11. Heat gun
12. Cooling fan for heat gun power controller
13. Compressed air line
14. Connections to heat gun
15. Digital temperature controller
16. Air brush – (spraying system)

Figure1. Spray drying set up used for synthesis of high surface are ceria and doped ceria.

carefully monitoring the effect of air flow-rate, temperature, concentration of solution, and atomization rate of solution in to the chamber on the particle size, conditions to obtain nano particles of ceria and doped ceria were established. Based on theseresults, $Pr_xCe_{1-x}O_2$, with x=0, 0.03, 0.1, and 0.20, were synthesized. Homogeneity, particle size and reduction temperature of these samples were compared with samples obtained by mixing and calcining the solid powders in appropriate concentrations (direct calination). The system has since been employed to synthesis a variety of doped cerias including gadolinium doped cerias. The powders were used as precursors for the synthesis of cermets (a SOFC anode material) and oxygen conducting electrolytes.

2. Characterization of Nano-particles

The effect of synthesis and calcination conditions on the homogeneity, strain and particle size (surface area) was determined using x-ray diffraction (XRD). XRD results show that all the samples, synthesized by either direct calcination or spray drying, have fluorite structures typical for CeO_2. Particle size and strain was measured from the peak broadening in XRD spectra, using Williamson-Hall equation. The effect of temperature on the particles size for various samples is shown in Figure 2. From these numbers, it is safe to conclude that the particle size increase with calcination temperature for all samples. On the other hand, particle size in directly calcined samples, 500 ºC, was slightly larger (20-27nm) than for the spray-dried samples (12-15 nm).

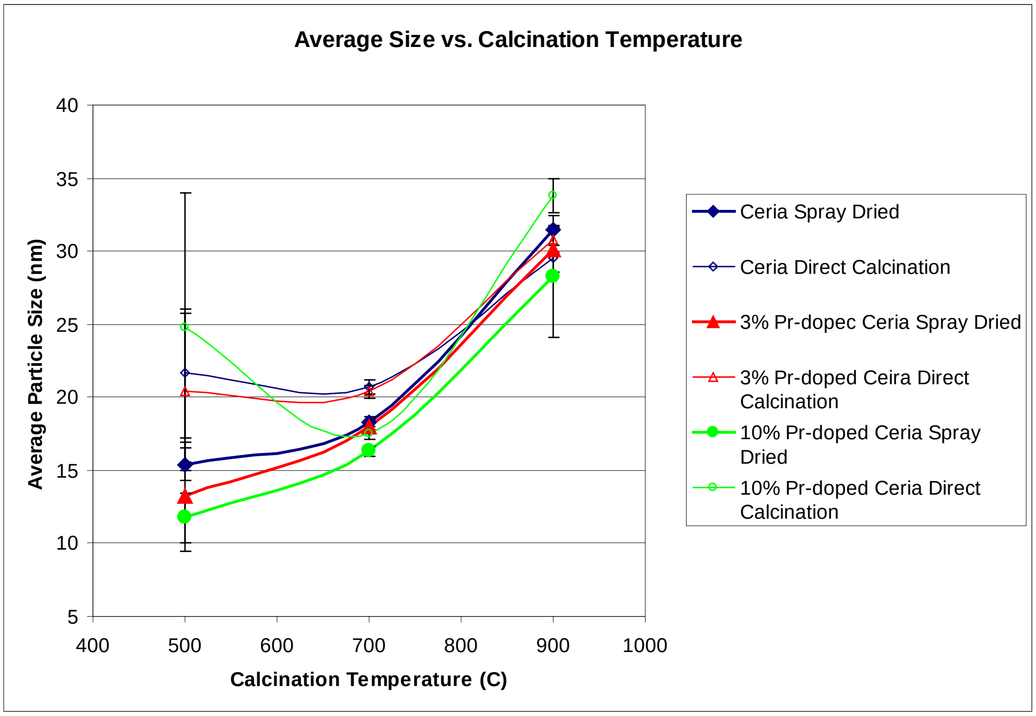


Figure2. Comparison of average crystallite size vs. calcination temperature for directly calcined and spray-dried followed

Heterogeneity in the doped samples could not be measured by XRD except for 10% samples, where existence of Pr_2O_3 after reduction of directly calcined samples indicate a Pr did not make a solid solution with Ceria. Instead, phase separated particles of PrO_2 were present in the sample that reduced to form stable Pr_2O_3 when heated at high temperature. HRTEM data confirmed that although local heterogeneity was present in 3% and 10% Pr doped samples synthesized by eithertechnique, the highest local compositional variation was present for 10% Pr doped samples synthesized by direct calcination. These samples were further studied to determine inter-granular and intra-granular heterogeneity using spatially resolved (0.5 nm) EELS.

High resolution imaging and electron energy-loss spectroscopy were performed using FEI-TECNAI F20 environmental TEM and JEOL 2010F microscopes, operated at 200kV. The contribution from Pr in doped oxide samples was obtained using the spectra from pure CeO_2 for calibration.

HREM images from pre-calcined (Figure 3a) and calcined (Figure 3b) Pr-doped CeO_2 samples show that the particle size increases after calcination. EELS spectra collected from individual grains were processed to determine the compositional heterogeneity by measuring relative intensity ratios of Pr to Ce signals. Several steps were required in the Pr background removal procedure because of the overlap between the Ce (at 890eV) and Pr (at 920 eV) signals. Higher variation in the distribution of Pr was observed in the pre-calcined sample compared to the calcined sample. From measurements of 20 particles it can be concluded that the samples became more homogeneous after calcination.

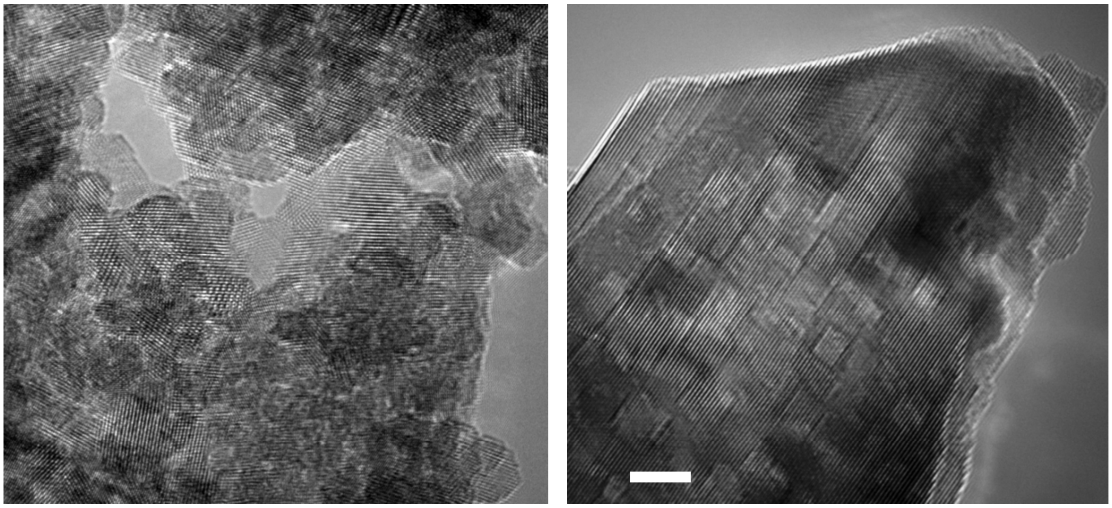


Fig.3. Typical HREM images recorded from (a) pre-calcined and (b) post-calcined (700°C) Pr-doped CeO2 sample showing an increase in particle size after calicination.

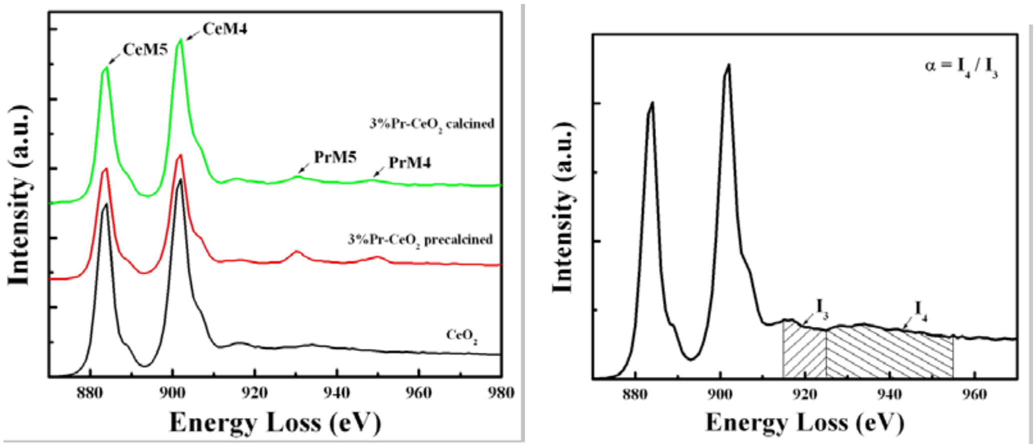


Fig.4. (a) EELS spectra from individual particles of pure CeO$_2$, precalcined and calcined Pr-doped samples respectively, (b) energy windows used to obtain intensity ratios.

3. Ex-situ and In situ Measurement of Redox properties

The relationship between doping level for Pr, Gd, Pr-Gd and reducibility was obtained using thermogravimetric analysis (TGA). Our measurements indicate that reduction temperature reduces as the percentage of doping in the samples is increased. Our experimental as well as theoretical result show that samples co-doped with Pr and Gd have best redox properties at low temperatures. Also, a direct comparison of the reduction temperature for direct calcined and spray-dried samples show that the latter reduce at lower temperatures (~50 ºC) compared to the former.

In situ redox experiments performed using Tecnai F20 E(S)TEM confirmed the general trends obtained from TGA measurements. However, the reducibility and redox properties were observed to vary within sample regions of doped particles due to local compositional variations as measured using the EELS data as explained above. The effect of local compositional variation on reduction temperature was most clear for 10% directly calcined sample (Figure5). Reduction of Ce is easily visible in EELS spectra as the intensities of Ce-M$_{4,5}$ ratios reverses as the Ce^{3+} concentration increases in the sample. The EELS data collected from two regions in the same sample recorded at 650 C show that the region with high Pr content (Figure5, top) is reduced while the region with low Pr concentration is not (Figure5, bottom). Detailed quantitative analysis is currently being performed.

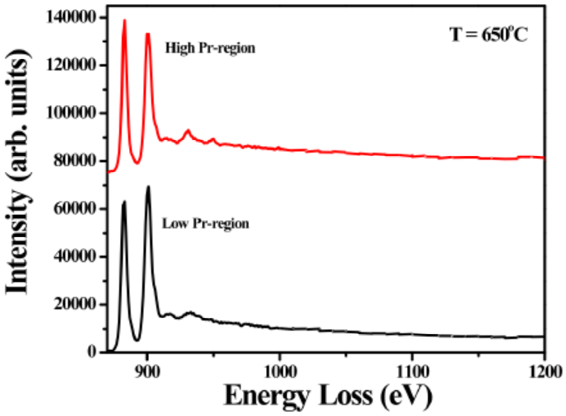


Figure5. EELS data collected from two regions of the same sample at 650 C showing different level of reduction dependent upon the Pr concentration.

4. Metal-Ceramic Interactions under Reducing Conditions

The anode of a solid oxide fuel cell is composed of cermet composite consisting of an ion conducting oxide and an electron conducting metal. For this project we selected doped ceria as the ion conducting oxide and nickel for the electron conductor. The behavior of these metal-ceramic composites were investigated using in situ environmental transmission electron microscopy. Two different structures we investigated; Ni nanoparticles supported on doped ceria and a coarser grained cermet (component particles approaching one micron).

4.1 Ni Nanoparticles on Ceria

Doped ceria was fabricating using the spray drying system described above and Ni metal was then loaded onto the ceramic using a traditional impregnation technique. In situ studies on reduction processes in praseodymium-doped ceria and nickel-loaded doped ceria nanoparticles showed that the presence of pit-like defects on the oxide nanoparticles resulted in amorphization during reduction. A hydrogen-spillover phenomenon in nickel-loaded praseodymium-doped ceria (PDC) was directly observed. Localized reduction of ceria in a H_2 atmosphere was observed and attributed to gas- nickel-ceria interactions at the three-phase boundary. H_2 was dissociatively adsorbed onto the the Ni at about 400oC and the proton subsequently spilled onto the ceria support resulting in localized reduction. The spatial extent of the localized reduction zones was experimentally determined to be about 20 nm in this case. The spillover mechanism was interpreted in terms of surface diffusion properties of atomic hydrogen and oxygen species. Further details can be found in the published work [5.6.10].

4.2 Anode Cermet Preparation and In Situ Observation

The spray drying techniques were employed to prepare coarse grain model anode cermets. The cermets are prepared by combined NiO powder with gadolinium doped ceria. Both oxides were prepared by spray drying. The two powders were then ball milled and then pressed into cylindrical pellets using a hardened steel die under uniaxial compression (180 MPa) at room temperature. The green bodies were sintered in air atop platinum foil at 1350 °C in for 12 h. The resulting cermic composite consisting of GDC and NiO is a precursor to the cermet. To convert this precursor to a cermet, the material must be reduced in flowing hydrogen at temperatures up to 800^{o}C to reduce the NiO to Ni metal. In situ electron microscopy was employed to follow the changes taking place in the materials during the reduction process. The large volume change associated with the NiO reduction process give rise to a porous structure consisting of Ni particles and GDC particles. Ni metal was observed to migrated over the surface of ceria grains during the reduction and the NiO reduction process was not uniform over the entire sample. Preliminary results from this work have been reported in a number of conference proceedings. Full detailed will be published in the future [9].

5. Modeling vacancy diffusion in Pr-doped Ceria

We have developed a theoretical model to predict the ionic conductivity in single crystal doped ceriasDensity functional theory (using VASP) was employed to calculate the activation energy for different diffusion paths in a variety of doped cerias and co-doped cerias. Ae have Kinetic Lattice Monte Carlo (KLMC) model was then used to model the oxygen vacancy diffusion in the crystal in order to determine the ionic conductivity. For Pr-doped ceria, oxygen vacancy formation and migration were investigated at first, second, and third nearest neighbor positions to a Pr ion. The second nearest neighbor site is found to be the most favorable vacancy formation site. Vacancy migration between first, second, and third nearest neighbors was calculated (9 possible jumps), with activation energies ranging from 0.51 eV to 0.88 eV for first-nearest-neighbor jumps (Figure 6). Overall, the presence of Pr significantly affects vacancy formation and migration, in a complex manner requiring the investigation of many different migration events any dopant has a complex effect on vacancy formation and migration. A variety of different dopants have been evaluated and the results are published in a series of references [2,3,4,6,7,8]. The model for GDC showed that doping levels of 10 – 20% gave the highest ionic conductivities in agreement with the best experimental observations. Interestingly, co-doping GDC with Pr, lead to higher ionic conductivity.

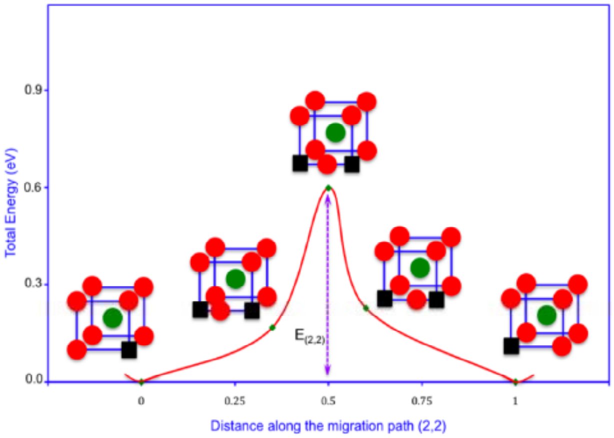


Figure 6. Schematic for the activation energy barrier for the oxygen vacancy migration form 2NN to 2NN position with respect to the praseodymium atom in Pr-doped ceria. Red and green balls represent oxygen and praseodymium atoms respectively. Black box represents

Major Accomplishments:

1. Built a chamber for nano-powder synthesis by spray drying that can be used for nano-particle synthesis of any composition from salt solutions.
2. Established doping levels for best redox properties.
3. Nanoscale measurements of formation of reduction zone at TPB for Ni-doped ceria cermet due to hydrogen spillover on Ni.
4. Developed Kinetic lattice Monte Carlo (KLMC) model to predict the oxygen ionic conductivity in single crystals of doped ceria.
5. Investigate the activation processes in model ceria based cermets for solid oxide fuel cell anodes.

List of Journal Publications:

1. V. Sharma, K.M. Eberhardt, R. Sharma, J.B. Adams, P.A. Crozier, (2010) "A Spray Drying System for Synthesis of Rare-Earth Doped Cerium Oxide Nanoparticles", Chemical Physics Letters, 495 280-286.

2. P.P. Dholabhai, J.B. Adams, P. Crozier, R. Sharma, (2010) "Oxygen Vacancy Migration in Ceria and Pr-Doped Ceria: A DFT plus U Study", Journal of Chemical Physics, 132 8.

3. P.P. Dholabhai, J.B. Adams, P. Crozier, R. Sharma, (2010) "A Density Functional Study of Defect Migration in Gadolinium Doped Ceria", Phys. Chem. Chem. Phys., 12 7904-7910.

4. Pratik Dholabhai, James Adams, Peter Crozier and Renu Sharma, (2011) "First-principles Study of Defect Migration in RE-doped Ceria (RE = Pr, Gd)", MRS Online Proceedings Library, 1311, mrsf10-1311-gg05-08 doi:10.1557/opl.2011.158

5. V. Sharma, P.A. Crozier, R. Sharma and J.B. Adams, (2012) "Direct Observation of Hydrogen Spillover in Ni-Loaded Pr-Doped Ceria ", Catalysis Today **180**(2) 2-8.

6. P. P. Dholabhai, S. Anwar, J. B.Adams, P. A. Crozier, R. Sharma, (2011) "Kinetic lattice Monte Carlo model for oxygen vacancy diffusion in praseodymium doped ceria: Applications to materials design ", Journal of Solid State Chemistry 184(4): 811-817.

7. P. P. Dholabhai, J. B.Adams, P. A. Crozier, R. Sharma, (2011) "In search of enhanced electrolyte materials: a case study of doubly doped ceria", Journal of Materials Chemistry, 21(47): 18991-18997.

8. P. P. Dholabhai, S. Anwar, J. B.Adams, P. A.Crozier, R. Sharma (2012) "Predicting the optimal dopant concentration in gadolinium doped ceria: a kinetic lattice Monte Carlo approach." Modelling and Simulation in Materials Science and Engineering **20**(1): 13.

9. Vaneet Sharma, Renu Sharma, Qianlang Liu and Peter A. Crozier, "In Situ Nanostructural Changes in Ni-GDC Anode for Solid Oxide Fuel Cells Observed Using an Environmental Transmission Electron Microscope" (in preparation)

Published Conference Proceedings

1. V. Sharma, Q. Liu and P.A. Crozier, "In Situ Nanostructural Changes in Ni-GDC Anode for Solid Oxide Fuel Cells Observed using an Environmental Transmission Electron Microscope", Microscopy and Microanalysis 18 Suppl. (2) (2012) CD.
2. 2**.** V. Sharma, R. Sharma and P.A. Crozier, "In-situ Observations of Interfacial Interactions Between Ni Catalyst and Pr Doped Ceria Support During Reduction", Proc. 17th International Microscopy Congress, (2010) M19.27 CD.
3. 3**.** V. Sharma, R. Sharma and P.A. Crozier, "In Situ Observations of Interfacial Interactions between Ni Catalyst and Pr Doped Ceria Support During Reduction", Microscopy and Microanalysis 16 Suppl. (2) (2010) 304CD.
4. 4**.** V. Sharma, K. Eberhardt, R. Sharma and P.A. Crozier, "Nanoscale Compositional Heterogeneity in Pr-Doped CeO2", Microscopy and Microanalysis 15 Suppl. (2) (2009) 730CD.

Participants and Human Development:

The grant provided full or partial support for graduate students, a postdoc and faculty summer salary. Ph.D. student Vaneet Sharma was fully support for the duration of his Ph.D. and was responsible for most of the experimental work performed on the project including materials synthesis and in situ electron microscopy. Vaneet graduated with a Ph.D. in the Fall of 2011 and currently works at Intel. Katie Eberhardt was fully supported as a masters student during the project and was involved in the design and fabrication of the spray drying system. She graduated and currently works at Intel. Ph.D.

student, Santhosh Chenna, was supported for a year on the grant and worked on in situ electron microscopy. He graduated in the summer of 2011 and currently works at Evans Analytical. Undergraduate student William Bowman was partially support directly from the grant for about 5 months and worked on preparation of electrolyte materials. He obtained a FURI scholarship from ASU and continued to work on the project. He is currently a Ph.D. students at ASU working with Drs Crozier and Sharma on ceria-based electrolytes. Dr. Pratik Dholabhai **was supported full time as a post-doctoral fellow for almost 3 years. He worked on the density functional theory and kinetic Monte Carlo codes to model oxygen ion conductivity in doped cerias. He is currently a research scientist at Los Alamos National labs. Drs Sharma and Crozier supervised the students for the duration of the project and Dr. Adams supervised Dr. Dholobai**