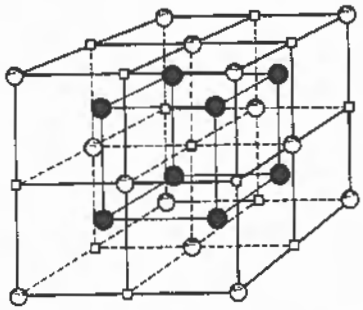
Hydrothermal Synthesis and Applications of Ceria-Based Oxides

Crystal D. Goshorn Literature Seminar October 23, 2003

Ceria-based oxides have a variety of uses ranging from UV filters in sunscreen[1] and solid oxide fuel cells (SOFC)[2-5] to three way catalysts (TWC)[6,7]. The main focus of current research lies in the applications for SOFC's and TWC's. Ceria-based oxides crystallize in the cubic fluorite structure shown in Figure 1[8].



Cerium- white atoms, face centered cubic
Oxygen- dark atoms, tetrahedral holes
Interstitial sites- squares, unoccupied octahedral holes

Figure 1

One of the reasons that ceria-based oxides are studied is due to their conductive properties. Conductivity in these oxides results from the creation of oxygen vacancies. These oxygen vacancies can either result from maintaining electroneutrality after the reduction of Ce(IV) to Ce(III) (eq. 1) or compensating for substitutions of cations with lower vacancy, such as trivalent cations (M) (eq. 2). The subscripts in the equations indicate the position of the atoms with respect to the lattice. Each bullet indicates a positive charge compared to the charge found at that site in the normal lattice. The apostrophe indicates a negative charge.

$$2Ce_{Ce} + O_O \rightarrow 2Ce'_{Ce} + V_O^{\bullet\bullet} + \frac{1}{2}O_2 \qquad \textbf{Eq. 1}$$

$$xMO_{1.5} + (1-x)CeO_2 \rightarrow xM'_{Ce} + \frac{1}{2}xV_O^{\bullet\bullet} + (1-x)Ce_{Ce} + (2-\frac{1}{2}x)O_O \qquad \textbf{Eq. 2}$$

Increasing the number of oxygen vacancies increases the conductivity of the sample up to a certain point. After the conductivity maximizes, defect associations start to form which inhibit anion migration.[9] The reduction of cerium as well as the introduction of dopants also affects the oxygen storage capacity of these materials. The facile electron flow from Ce(IV)↔ Ce(III) allows oxygen storage and release. Doping with lower valence ions decreases the activation energy for migration while smaller radii elements increase the oxygen storage capacity.[10]

Synthesis of these mixed oxides can be a quite complex process. Previous synthesis methods include solid-state synthesis and co-precipitation. These

methods have drawbacks including high temperatures, lengthy protocols, non-homogeneity of particles, and lack of thermal stability[9]. The hydrothermal synthesis method operates at lower temperatures than solid-state methods while producing stable, homogeneous nanometer scale particles[9,11]. This method is not a new technique and has been used for quite some time in geological circles and for the synthesis of zeolites[9]. The hydrothermal synthesis method commonly uses an autoclave, Figure 2[11], while there has been recent research dedicated to implementing a continual flow system, Figure 3[12], as well as branching into solvent-free methods[13].

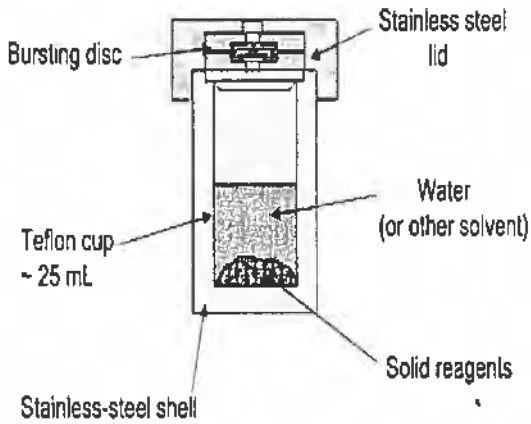


Figure 2

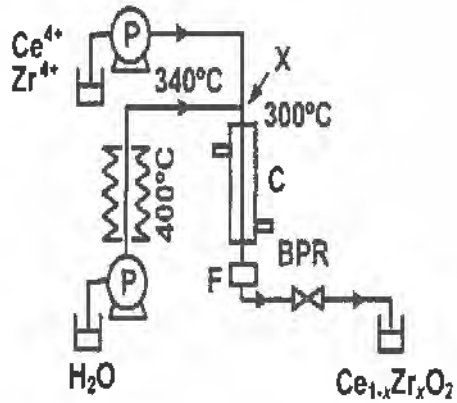


Figure 3

The greatest advantage that the hydrothermal synthesis method has to offer is that it allows the production of new pure materials as in the case of $Ce_{1-x}Fe_xO_2$. The cerium-iron oxides are examples of new materials that are of interest as three way catalysts. Several other studies have been preformed using ceria-based materials as possible TWC's[14-16]. The oxygen storage capacity of these compounds is much improved over pure CeO_2[10]. $Ce_{1-x}Gd_xO_{2-\delta}$ is thought to be the material with the most promise for use in SOFC's. It exhibits conductivity over two orders of magnitude greater than pure CeO_2[17]. This material is proposed as a better material for use as the electrolyte in SOFC's. Other possible materials for SOFC's have been studied.[18,19] These systems as well as systems of other ceria-based oxides have been studied.

Synthesis of new CeO_2 compounds is feasible using the hydrothermal synthesis method. These products exhibit increased conductivity as well as other improved properties which makes them useful in industrial applications.

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