

Cerium-based oxide coatings



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ABSTRACT

Cerium-based oxide compounds are known for their wide range of applications in catalysis, corrosion prevention, electrochemical cells, photocatalysis, UV absorbers, biomaterials, microelectronics, optical devices, thermal coatings, and glass abrasives. The technological applications of these materials are possible due to a combination of the electronic structure of Ce and the size effects at the nanoscale. In particular, reversible transformation between the Ce(III) and Ce(IV) oxidation states on the surface of cerium oxides is critical to the functionality and potential uses of the materials. In this paper, the main technological applications of cerium-based oxide coatings are reviewed based on the work done to date. Special interest is placed on the emerging trends.

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Introduction

Rare earth elements are important constituents of permanent magnets, rechargeable batteries, anti-corrosion coatings, and catalysts [1,2]. Among the rare earths, cerium is the most abundant, comprising 66 ppm of the earth's crust, comparable to copper (68 ppm) and more abundant than cobalt (29 ppm), lead (13 ppm), or silver (0.08 ppm) [1–3]. The classification as “rare” is related to the lack of concentrated ore bodies. Rare earths are typically low assay concentrations with specific ratios in a variety of ores; cerium and yttrium are the most commonly detected elements. Demand of some of the minor constituents in rare earth containing ores, such as neodymium, have produced an excess of cerium and lanthanum [1,2]. In addition to the availability of cerium, the stability of Ce(III) and Ce(IV) oxidation states enables the formation of Ce(IV) molecular complexes that results in a relatively low cost to separate Ce from other lanthanide elements contained in the ore [4]. While Ce metal has been used as an alloying agent, the high electromotive force value of the Ce(III)/Ce(IV) redox potential results in the formation of cerium compounds, especially oxides.

Cerium-based oxides are very attractive materials for technological applications such as catalysis [5–15], corrosion prevention [16–48], electrochemical cells [9,49–51], photocatalysis [52–58],

UV-absorbers [59–61], biomaterials [62–64], microelectronics [15,65–67], optical devices [66–68], thermal barriers [30,69–71], and glass abrasives [72–75]. This wide range of applications is due to the particular physical and chemical properties that are related to the electronic structure of Ce [6,52,62,63,76–79].

The electronic structure of isolated cerium metal is $[\text{Xe}]4f^{15}d^{1}6s^2$. The small energy difference between the inner 4f electron and the outer valence electrons allows cerium to have two stable valence states, 3+ or Ce(III) and 4+ or Ce(IV) $[\text{Xe}] 4f^1$ [76,78,80].

In aqueous solutions, cerium possesses a large reduction potential of approximately -2.3 eV vs NHE [4]. The one-electron redox couple Ce(IV)/Ce(III) potential is reported to be approximately $+1.7$ eV [4,81–83]. These potentials make Ce a strong reducing agent and Ce(IV) a strong oxidizing agent. The electronic structure of cerium was controversial as it related to the nature of the 4f orbital in Ce-based compounds; e.g. CeO₂ was described as the $[\text{Xe}] 4f^0$ configuration (“pure” tetravalent Ce) with the O 2p valence band completely filled. However, experiments have shown a mixture of $[\text{Xe}] 4f^0$ and $[\text{Xe}] 4f^1$ configurations in nanostructured cerium dioxide [84]. More recent work has demonstrated that the cerium atoms in CeO₂ must exist in the 4+ oxidation state, but the presence of any missing lattice oxygen atoms in the highly reducible oxide implies the existence of two Ce³⁺ ions close to each vacancy [6,76,85–87].

Among the different properties of cerium-based oxides, the ability to undergo oxidation–reduction cycles between Ce(III) and

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Ce(IV) species is perhaps one of the most important. Cerium redox reactions are related to the presence of oxygen vacancies in cerium oxides that can be easily formed, diffused or removed, particularly at surfaces of nanostructured materials [8,13,76,86]. A decrease in size of CeO₂ nanoparticles has been related with an increase of lattice constants or lattice relaxation associated with an increase of the oxygen vacancy content [88]. Due in part to the high reactivity of surfaces, recent investigations have shown that the redox properties of nanostructured cerium oxides are not only highly dependent on crystallite size but also on crystallite morphology [89]. Theoretical studies and experimental work have demonstrated that oxygen vacancies are more likely to form on (100) planes than (110) planes and that vacancies on (110) planes are favored over those on (111) planes [5,89,90]. Correspondingly, nanostructured cerium-based oxides fabricated with (100) and (110) preferred orientations have shown enhanced catalytic properties at room temperature compared to bulk compounds exhibiting (111) texture not only because of their size but also because of the increase in oxygen vacancies associated with the crystallographic orientations [89].

The ease of formation of oxygen vacancies in cerium oxides at the nanoscale results in mixed valence compounds of the form CeO_{2-x} [14,65,78,86]. Therefore, the properties of these oxides are highly dependent on the electronic structure that results from processing conditions that affect the type and concentration of defects [9,91]. For example, the band structure of stoichiometric CeO₂ is characterized by an energy gap of ~6 eV between the occupied O 2p states and the unoccupied Ce 5d states with a narrow 4f⁰ band in between with an energy gap of ~3 eV. The partially reduced oxide CeO_{2-x} is represented by a highly-localized and partially filled f band split-off below the unoccupied f states with an energy gap of ~2 eV. The fully reduced oxide, i.e., Ce₂O₃, is similar to the partially reduced oxide, but the empty Ce 4f band and the Ce 5d band merge into a conduction band as shown in Fig. 1 [6,87]. Consequently, a detailed understanding of the electronic band structure and its relationship with properties and structure is very important in identifying the mechanisms governing the potential applications of the nanostructured cerium-based materials. Hence, cerium-based nanoparticles, nanorods, and thin films can be fabricated in different sizes and crystallographic orientations, providing the potential to control the oxygen vacancies and therefore the Ce(III)/Ce(IV) ratio. While a few important technological aspects from the various applications of Ce-based materials are mentioned, this paper is focused on applications of cerium-based oxide coatings.

In the following section, a short summary of the most important techniques to produce cerium-based oxide coatings is presented.

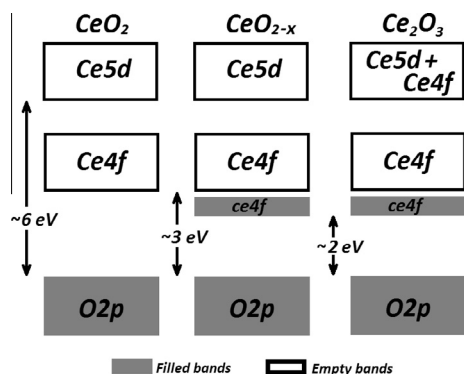


Fig. 1. Band structure of cerium oxides (adapted from [85]).

Techniques to produce Ce-based oxide coatings

The methods for producing cerium-based oxide coatings can be divided into two main categories, liquid phase processing [16–19,27–29,31,48,52,57,58,92] and vapor phase deposition [15,68,93–96]. For the liquid solution approaches, aqueous chemical conversion methods are most commonly used to produce Ce-based coatings [16–19,27–29,31,48,52,57,58]. However, Ce-based films have also been prepared by sol-gel [97,98], hydrothermal precipitation [99], plasma electrolytic immersion [30], electroplating [92], and spray pyrolysis [66,100] processing techniques. Recently, phase stability diagrams for cerium species in aqueous systems (H₂O₂/O₂) were reexamined to define the Ce(III) and Ce(IV) domains as a function of pH and solution oxidizing potential [81–83]. These limits describe conditions for the formation of cerium compounds, which can lead to more economically viable and scalable liquid phase processes. For vapor phase deposition, magnetron sputtering has been the most actively investigated technique to produce homogeneous Ce-based thin films [15,50,93,94]. In addition, other vapor phase techniques such as pulsed laser deposition [96,101], atomic layer deposition [95], metal-organic chemical vapor deposition [102], and electron beam evaporation [65,68] have been also used to form Ce-based thin film coatings. Although the coatings discussed in the present review are predominately focused on 2D nanostructures, the preferred fabrication method for Ce-based nanoparticles (0D) and nanorods (1D) is through hydrothermal precipitation routes [5,59,90,103].

Applications of Ce-based oxide coatings and their relationship with electronic structure

Cerium oxides have been investigated for more than a century for applications in catalysis, optical devices, UV absorbers, and electrochemical cells, but the properties and specific mechanisms were not fully characterized [9,62,67,76,104,105]. Interest in cerium oxides increased significantly in recent decades after incorporation into three-way catalysts for automotive pollution control systems. However, noble metal-CeO₂ interactions decrease with time, which, in turn, deactivated the catalysis function and led to a lower oxygen storage capacity [104]. This problem was overcome by replacing the CeO₂ by a mixture of CeO₂ and ZrO₂. The introduction of CeO₂-ZrO₂ mixed oxides was a success in three-way catalysis technology compared to Pt/Al₂O₃ [104,106]. This application is perhaps one of the most important for rare earth oxides since it simultaneously converts CO, NO_x, and unburned hydrocarbons into CO₂, N₂, and H₂O [104]. Due in part to this interest, fundamental research in the electronic structure of Ce was conducted [78,79,84,107,108]. Multiple effects are attributed to cerium oxide in three-way catalysis systems including promotion of noble metal dispersion, increase in the thermal stability of the supports, promotion of water-gas shift reaction, and oxygen buffering. The latter is utilized in the reversible reaction CeO₂ ↔ CeO_{2-x} + (x/2) O₂ that allows these oxides to store and release O₂ in both oxidizing or reducing conditions, assisting in the simultaneous oxidation of CO to CO₂ while reducing the NO_x to (x/2) O₂ [104,106]. Therefore, the Ce(IV)/Ce(III) redox cycle is the key aspect of Ce-based oxides in three-way catalysis.

Cerium oxides were also widely investigated as possible materials for thermal barrier coatings (TBCs) due to the high melting point, high thermal expansion coefficient ($\alpha \approx 13 \times 10^{-6} \text{ K}^{-1}$ from 293 to 1500 K), and relatively low thermal conductivity ($\lambda \approx 2.77 \text{ W m}^{-1} \text{ K}^{-1}$ at 1273 K) of the material [69,70]. Although CeO₂ can perform as a thermal barrier coating, its disadvantages include stoichiometric changes due to the reduction of CeO₂ into Ce₂O₃ at high temperature and an increase in the sintering rate

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