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Electrochemical and catalytic applications of cerium(IV) oxide

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Abstract

Cerium(IV) oxide is one of the most important rare earth metal oxides owing to its high oxygen storage and release capacity, as well as thermal and mechanical stability. Its various applications range from sensors, solid oxide fuel cells and supercapacitors to the most important catalytic application in three-way catalytic converters, oxidation of volatile organic molecules, water-gas shift reaction, etc. This short review article gives a brief introduction to rare earth metals, then describes in detail the properties of cerium(IV) oxide and ways to improve them, as well as presents an overview of the most important and current applications of cerium(IV) oxide. Finally, it gives an overview of the results obtained by our group regarding pure and doped cerium(IV) oxide for various applications.

Keywords: cerium(IV) oxide, doping, nanotechnology, catalysis.

1. Introduction

Rare earth elements are a group of 17 chemically similar elements and include lanthanides, scandium and yttrium. They are all silver, silvery-white, or grey lustrous metals and are usually divided into light (from lanthanum to gadolinium) and heavy (from terbium to lutetium and yttrium), depending on the electronic configuration, which influences their respective properties. Although the name suggests the opposite, rare earth metals are relatively well distributed in the Earth's crust, but very rarely concentrated in recoverable ore deposits. Due to the similarities in structure, they naturally appear together in minerals and are found with non-metals, especially strong electronegative elements such as oxygen or fluorine. Rare earth metals and their compounds are widely used in various industries, and are thus used in metallurgy, glass and ceramic polishing, for the production of electronic components, as permanent magnets, and as catalysts in technological chemical processes, the automotive industry and petroleum refining. [1, 2] The most abundant of rare earth elements is cerium, which has two stable oxidation states, Ce^{3+} and Ce^{4+} , and can therefore form two types of oxides, Ce_2O_3 and CeO_2 . Cerium (IV) oxide possesses a higher application value and has therefore been the subject of considerable research in recent years. [3, 4]

2. Cerium(IV) oxide

Cerium(IV) oxide or ceria (CeO_2) has a fluorite type crystal structure with space group $\text{Fm}\bar{3}\text{m}$ in which ceria cations form the face centered cubic cell, while the oxygen anions occupy the tetrahedral interstices (Figure 1). Each cerium cation is coordinated by eight neighboring oxygen anions and each oxygen anion is coordinated by four neighboring cerium cations. This structure is stable over the whole temperature range from room temperature until the melting point. [5]

Pure stoichiometric ceria has a pale yellow color, which is assumed to be due to Ce(IV)-O(-II) charge transfer. [5] As already mentioned, cerium can be chemically present

in two stable valence states, Ce (IV) and Ce (III), and the special feature of ceria fluorite lattice is that it can tolerate a considerable reduction of Ce^{4+} to Ce^{3+} (Eq. 1) without any structural changes, particularly at high temperatures.



Such nonstoichiometric ceria $\text{CeO}_{2-\delta}$ ($0 < \delta < 0.5$) has blue color and can even turn black when largely nonstoichiometric. [4, 5]

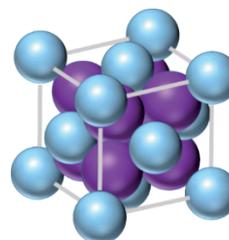
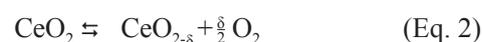


Figure 1. Ceria unit cell: Cerium cations (blue spheres) form a plane-centered cubic lattice, while oxygen anions (magenta spheres) occupy tetrahedral interstices.

When CeO_2 is further reduced, it forms the hexagonal cerium sesquioxide Ce_2O_3 with a $\text{P}\bar{3}\text{m}1$ space group. As a result of the ease with which Ce^{4+} may be reduced to Ce^{3+} , oxygen is released as a compensatory effect, resulting in mixed ionic electronic conductivity (MIEC) of ceria (Eq. 2). [6, 7]



In the course of this process oxygen vacancies are formed in the crystal lattice. The Ce^{3+} can easily be reoxidized by oxygen uptake, which makes ceria a suitable material for redox related catalytic applications or oxygen buffers. [7, 9] Good catalytic activity of CeO_2 can mostly be attributed to the easy shift between Ce^{3+} and Ce^{4+} oxidation

states, creation of oxygen vacancies and thereby high oxygen mobility and oxygen storage capacity (OSC) within the ceria crystal lattice. [5, 6]

Oxygen vacancies defects are prone to change depending on physical parameters such as temperature, oxygen partial pressure, doping of ceria with foreign ions, electrical field or surface stresses. Nevertheless, oxygen vacancies are the most important feature of ceria and they greatly influence its electronic and chemical properties. [6]

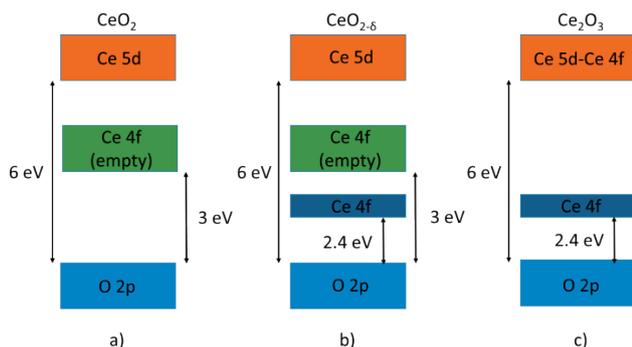


Figure 2. Schematic band diagram for (a) stoichiometric CeO_2 , (b) partially reduced CeO_{2-x} and (c) Ce_2O_3 .

Figure 2 shows the differences in electronic structure between cerium(IV) oxide, partially reduced cerium(IV) oxide and cerium(III) oxide. The electronic structure of CeO_2 consists of an O 2p based valence band and a Ce 5d based conduction band, between which lies an empty and narrow Ce 4f band (Figure 2a). When an oxygen ion leaves the ceria crystal lattice, a neutral species $\frac{1}{2} \text{O}_2$ is formed, while the two residue electrons become localized at the two nearest cerium sites. The electron at such cerium site is inclined to occupy the empty Ce 4f state, which causes the split of the Ce 4f band into two sub-bands: an empty and a full Ce 4f band (Figure 2b). When all Ce^{4+} ions are reduced to Ce^{3+} , Ce_2O_3 is formed. The electronic band structure of Ce_2O_3 is similar to that of partially reduced ceria, in which the empty Ce4f band and the Ce5d band have fused into the conduction band (Figure 2c). [7, 8, 9]

2.1. Doping

Another way to promote oxygen vacancies formation in cerium(IV) oxide is doping of ceria with elements having lower valence, such as transition metals. Doping is actually the introduction of extrinsic defects into the ceria crystal lattice by incorporation of foreign metal cations (Figure 3).

Studies have shown that doped ceria has better properties than pure ceria, which is attributed to the creation of additional oxygen vacancies and a reduced energy barrier for oxygen migration. Dopants can also modify and stabilize crystallite size and specific surface area of ceria nanoparticles, i.e. increase their resistance to grain growth at elevated temperatures, which is especially important

for catalytic applications. [10-12] High oxygen ion conductivities of doped ceria made it of great interest in use as a solid electrolyte in solid oxide fuel cells. [6]

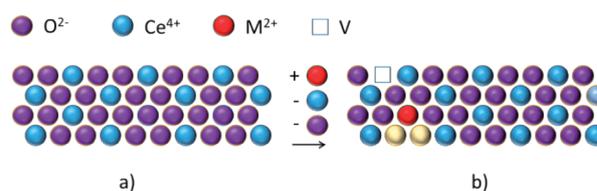


Figure 3. Modification of ceria crystal lattice (a) by incorporation of metal ions having lower valence. As a consequence of replacement of Ce^{4+} ion with M^{2+} ion, oxygen vacancy (V) appears (b).

Figure 2a shows that the band gap value between the O 2p and empty Ce 4f bands is around 3 eV, and that is the band gap value attributed to ceria according to literature. [13, 14] The value indicates that CeO_2 can strongly absorb UV light, but not visible light. Concerning possible photocatalytic and biomedical applications, it would be desirable to reduce the band gap value into the visible light region. Doping with different transition metals can help achieve this due to the aforementioned additional oxygen vacancies formation. When a transition metal ion (M^{2+}) substitutes Ce^{4+} , the number of oxygen vacancies V increases to preserve the charge neutrality (Figure 3). The two residue electrons further promote the reduction of Ce^{4+} to Ce^{3+} and the lattice strain increases. This is then reflected in electronic structure and the result is band gap reduction. In summary, the band gap reduction is due to increased crystal lattice disorder caused by defect states between valence bands and conduction bands. [14]

2.2. Nanocrystalline ceria

Nanotechnology is an ever emerging field which has gained much significance in many industrial branches. This is mainly due to the enhanced properties of nanosized materials in comparison to bulk materials. This phenomenon arises from the fact that nanoparticles of a material have a much larger specific surface area than the same bulk material, which can be better explained by figure 4. Atoms inside the material have all the possible chemical bonds satisfied, while the ones on the surface do not and therefore have higher energy than atoms on the inside, causing them to be more reactive because they tend to reduce their energy. For bulk materials, a far larger proportion of the atoms is situated in the interior, while for nanomaterials the number of surface atoms becomes significant. [16]

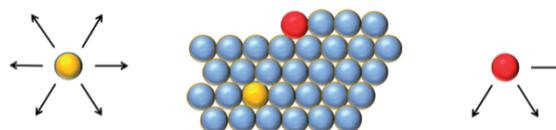


Figure 4. Surface atoms (red) due to unsatisfied chemical bonds have higher energy than atoms inside the crystal lattice (yellow).

Higher energy of surface atoms affects the morphology, reactivity, catalytic potential and other properties of nanomaterials. [16] The energy necessary for defect formation is reduced resulting in an increase in the level of nonstoichiometry and electronic carrier generation in nanocrystalline oxides. [6] Modern research is focused on the preparation, characterization and application of nanosized ceria because of its improved redox properties, transport properties and surface to volume ratio in comparison to bulk ceria. [6, 17]

3. Applications of ceria

The abundance of cerium, high mobility of oxygen vacancies and the reversible valence couple Ce^{4+}/Ce^{3+} make ceria a valuable oxygen storage material with extensive applications in various fields, such as catalysts, low-temperature water-gas shift (WGS) reaction, oxygen sensors, oxygen permeation membrane systems, fuel cells, electrochromic thin-film applications, ion batteries, etc. [7, 18] In the following chapters, few of these applications will be discussed in more detail.

3.1. Solid oxide fuel cells

Solid oxide fuel cells (SOFCs) are power generation systems which depend on electrochemical reactions to produce electricity in contrast to traditional Carnot restricted combustion cycles. High energy conversion efficiency is acquired by a clean, low pollution, reliable and adaptable technology making SOFCs the energy production system of the future. [19, 20]

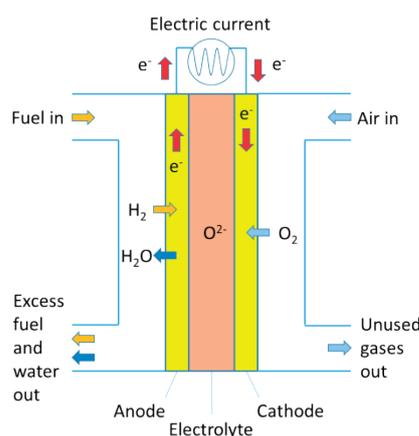


Figure 5. Solid oxide fuel cell components and working principle.

A solid oxide fuel cell consists of two porous electrodes (cathode and anode) between which lies a solid electrolyte (Figure 5). The electrolyte is an oxygen ion conducting material, which means it allows oxygen ions, but not electrons to pass through it. At the cathode, also called the air electrode, oxygen is supplied and it reacts with electrons from the external circuit to form oxygen ions which then migrate through the electrolyte to the anode (fuel electrode). The half reaction at the cathode is as follows:



The oxygen ions react with the fuel at the anode. The fuel can be pure hydrogen or a mixture of hydrogen and carbon monoxide, which can be obtained by internal reforming of a hydrocarbon fuel, e.g. methane, with the anode serving as a catalyst for this conversion. [21, 22] The products of the reaction when hydrogen is introduced at the anode are electrons and water vapor. The electrons (electricity) then flow through the external circuit to the cathode in order to keep the overall charge neutrality. The half reaction at the anode is the following:



Materials for SOFC components need to be carefully selected to enable the whole system to function properly. Some of the criteria are sufficient chemical and structural stability at operating and manufacturing temperatures; minimal reactivity and interdiffusion, as well as matching the thermal expansion between different components. The primary temperature range for SOFCs operation was between 900 and 1000 °C.

The advantages of such high temperatures were the reforming of hydrocarbon fuels and production of high quality heat for cogeneration. However, the reduction of this range to values between 650 and 800 °C opened up the possibility of using a wider range of materials for cell components, simplified the thermal management, enabled a faster start up and cool down, and resulted in less degradation of cell and stack components. The problem at lower temperatures is the decrease of electrolyte conductivity and electrode kinetics, which is why new materials for cell components are being designed and tested. [20, 21]

The most commonly used electrolyte material is yttria stabilized zirconia (YSZ) due to its sufficient ionic conductivity, chemical and thermal stability, and mechanical strength. The disadvantage of YSZ is low ionic conductivity below 750 °C. The use of scandia-doped zirconia, which has higher ionic conductivity, is one possible solution, but high cost of scandium and observed detrimental effects of ageing in scandia-doped zirconia hinder its use in commercial applications. [21, 23, 24] Electrolytes based on doped ceria exhibit a higher ionic conductivity than zirconia based materials ($0.025 (\Omega\text{cm})^{-1}$ for $Ce_{0.9}Gd_{0.1}O_{1.95}$ in comparison to $< 0.005 (\Omega\text{cm})^{-1}$ for zirconia, at 600 °C), and are also much cheaper due to the abundance of ceria in natural resources. [21, 25] Ceria is usually doped with gadolinium or samarium for its use in solid oxide fuel cells. [19-25] A serious drawback of ceria in this application is its easy reducibility at low oxygen partial pressures, i.e. the reduction of Ce^{4+} to Ce^{3+} and formation of oxygen vacancies, which leads to increasing electronic conductivity and potential mechanical decomposition under large oxygen chemical potential gradients common during SOFC process. [21, 25] This problem can be solved by decreasing the operation temperature below 600 °C, and doped ceria-based materials are being successfully implemented as electrolytes into modern commercial SOFCs, e.g. by Ceres Power Limited (UK). [21, 26]

In addition to being used as an electrolyte, cerium (IV) oxide can also be used in fuel cells as a barrier layer on the cathode to hinder its reaction with the YSZ electrolyte or it can be added to the cathode or anode material to serve as a catalyst. [27] A problem that occurs with hydrocarbon fuels is the accumulation of carbon on the anode which can deactivate and destroy the anode. In order to get around that problem, mixed conductivity and fuel direct oxidation or direct reforming electrocatalytic activity need to be secured. The formation of oxygen vacancies and the existence of electronic conductivity alongside ionic conductivity, which were its drawbacks in the use as electrolyte, are now the benefits of ceria for usage as anode oxidation catalyst. Ceria-based materials are proven to have higher resistance to carbon deposition, meaning that hydrocarbon fuels can be supplied directly to the anode without pre-reforming and purification. [27-30] Doping of ceria enhances the favorable properties, so a lot of research is focused on doped ceria materials, e.g. gadolinium-doped ceria (CGO) [31] and yttria-doped ceria (YDC) [32] The morphology of the catalyst also plays an important role as it can provide extra stabilization and enhance anode efficiency. Examples are work by Adijanto et. al which prepared Pd-CeO₂ core-shell systems that were found to be effective anodic catalysts for hydrogen and methane fuels with extra stability due to the core-shell structure [33] and research by Sun et al. who increased the efficiency of their anode with Ru-CeO₂ by achieving a porous flowerlike microsphere morphology of the CeO₂ support. [34] Research is also done on ceria-alumina systems, which are being extensively used in automotive catalysts where alumina is used as support for ceria catalyst. [27, 28, 35] Since it was noticed that the mechanical stability of ceria is not satisfying under SOFCs operating conditions [36], an idea arose to combine ceria and alumina in order to enhance the mechanical stability, as well as thermal stability of ceria without a negative impact on its ionic conductivity. In that way, CeAlO₃/CeO₂-Al₂O₃ nanosized-particle electrocatalyst was prepared which exists as CeAlO₃ in a reducing atmosphere and as ceria and alumina in an oxidizing atmosphere. [28]

3.2. Supercapacitors

Supercapacitors, also known as ultracapacitors or electrochemical capacitors, are electrical energy storage devices gaining prominence in recent years. One of the main reasons for the development of supercapacitors is the inevitable depletion of conventional energy sources, meaning that renewable sources will take over energy production industry. Since renewable sources mostly rely on natural phenomena like the sun or wind, which are unpredictable and unstable, renewable energy is not completely reliable. The solution is to find a good way to store the produced energy and then use it later when needed. [37, 38] In addition to batteries, supercapacitors are one of the possible solution methods, with their main advantages over batteries being higher power density, faster charging/discharging rate, good stability and longer cycle-life. [37, 39] A supercapacitor consists of two identical (symmetric supercapacitor) or different (asymmetric capacitor) electrodes with a separator in between them (Fig. 6). The

separator is an ion-permeable, but electrically-insulating material placed in an electrolyte which enables ion charge transfer between the electrodes. The material used for the separator depends on the type of the electrolyte used; ceramic or glass-fibers separators are used in aqueous electrolytes, while polymer or paper separators are used in organic electrolytes. [40]

There are a few possible classifications of supercapacitors: type of electrolyte (aqueous or organic), electrode material (carbon-based materials, transition metal oxides, and conductive polymers) and charge storage mechanism (electrochemical double layer capacitors - EDLCs, faradic pseudocapacitors, and hybrid capacitors. [41] Ceria/graphene composites are mainly studied as electrodes in pseudocapacitors. Pseudocapacitors store energy through rapid and reversible electrochemical redox reactions which occur on the interface between the electrodes and the electrolyte, making high specific surface area and high electrical conductivity crucial factors for electrode materials in high-performance pseudocapacitors.

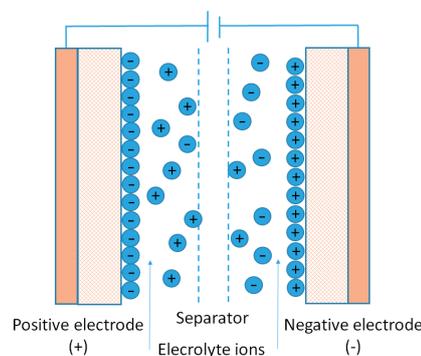
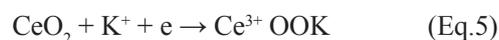


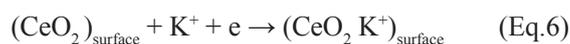
Figure 6. Schematic representation of electrical double-layer capacitor.

Graphene or other carbon based materials are in this case used as substrates for deposition of active materials and/or as current collectors which secure high capacitance and fast charge transfer of the electrodes. The active component is usually a metal oxide or a conductive polymer. As metal oxides are concerned, the metals used must have at least two oxidation states, which can coexist and be freely and easily interchanged. [40] Ceria has two stable oxidation states and an easy transition between the states is possible without the collapse of crystal structure. Per se, ceria can store charge electrochemically by Faradaic redox reactions or by non-Faradaic process through electric-double layers. For better understanding, equations 5 and 6 present the non-Faradaic and Faradaic process for a ceria electrode when KOH is used as electrolyte [42]:

Faradaic process:



Non-Faradaic process:



Both processes occur on the surface of the electrode and are therefore highly dependent on its specific surface area. The use of nanosized ceria instead of bulk one enhances the charge-storage performance due to the higher specific surface area of nanomaterials. Additional improvements can be achieved by doping. Ghosh et al. studied Zr doped ceria and reported on the enhancement of pseudocapacitive behavior of ceria due to incorporation of Zr ions into the ceria crystal lattice. Namely, doping promotes the formation of oxygen vacancies and the redox reaction between Ce^{4+} and Ce^{3+} ions, which induces higher Faradaic contribution to charge-storage. Furthermore, doping causes the reduction of average crystallite size and average particle size which in turn increases the specific surface area and improves the non-Faradaic contribution. [42]

3.3. Catalytic application

Ceria is extensively used as a heterogeneous catalyst in many technologically important processes. Traditional catalysts, namely noble metals are expensive, scarce in resources, sensitive to high temperatures and susceptible to poisoning. Cerium (IV) oxide is being imposed as a viable alternative because it has suitable properties like low cost, availability, low sensitivity to high temperatures and good resistance to poisoning, while at the same time enabling high conversions for certain types of chemical processes. Cerium (IV) oxide is used as a catalyst and promotor in three-way catalytic converters in car exhaust systems [35], for the conversion of water-gas, also known as synthesis gas - a mixture of carbon monoxide and hydrogen, to produce hydrogen for various industrial processes [43, 44], in self-cleaning ovens [45], and for the removal of atmospheric pollutants such as volatile organic compounds [14, 46].

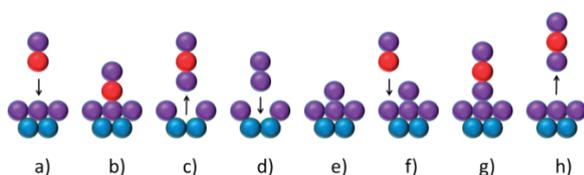


Figure 7. Carbon monoxide oxidation process in presence of ceria catalyst. Blue dots represent cerium atoms, magenta dots oxygen atoms and red dots carbon atoms.

The catalytic activity of ceria can be illustrated on carbon monoxide oxidation process (Figure 7). CO molecule is adsorbed onto the ceria surface (a). The ease of formation of oxygen vacancies facilitates the reaction between CO and surface oxygen (b). The formed carbon dioxide diffuses away leaving an oxygen vacancy (c), where a new oxygen molecule is then adsorbed (d). The presence of oxygen vacancy enables the reaction of the adsorbed oxygen molecule with the ceria surface, thereby weakening the bond between oxygen atoms in the molecule (e). Another CO molecule adsorbs on the surface (f), diffuses to the excess oxygen and reacts with it (g) and diffuses away from the surface (h). This particular reaction occurs in the

exhaust system of automobiles and ceria is commercially applied as a catalyst in this process. [47, 48] Hence, a more detailed explanation of automotive catalytic converters is due.

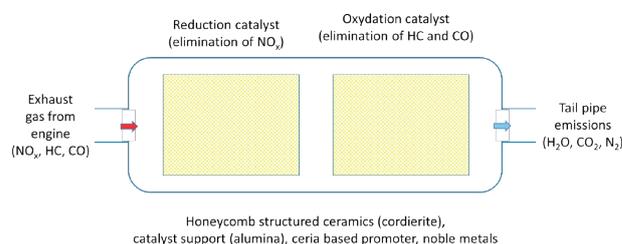


Figure 8. Basic components of a three-way catalytic converter.

Figure 8 shows the basic components of a three-way catalytic (TWC) converter in automotive exhaust systems. The term three-way pertains to the three types of pollutants it helps to reduce: nitrogen oxides (NO_x), carbon monoxide (CO) and hydrocarbons (HC). Basically, three reactions happen simultaneously inside the TWC converter: [35]

1. Reduction of nitrogen oxides into elemental nitrogen and oxygen
2. Oxidation of carbon monoxide to carbon dioxide
3. Oxidation of hydrocarbons into carbon dioxide and water

Therefore, three-way catalytic converters utilize two types of catalyst – a reduction and an oxidation catalyst. Both of them typically consist of a monolithic support which is usually made of cordierite and has a honeycomb structure insuring the best possible contact between the catalyst and exhaust gases. The honeycomb consists of channels whose inner surface is coated with the catalytically active material. This material is composed of a thermally stable support (most common being Al_2O_3), the active phase which are mainly noble metals (Pt and/or Pd for oxidation reactions and Rh for reduction reactions) and a ceria-based promoter (typically $Ce_xZr_{1-x}O_2$). The gas phase coming from the engine into the converter constantly and rapidly oscillates between lean (air-to-fuel ratio > 14.6) and rich conditions (air-to-fuel ratio < 14.6). In order to operate properly, a three-way catalytic converter must first reduce the NO_x compounds during rich conditions and then oxidize CO and HC during lean conditions. The main role of ceria is to act as oxygen buffer: reduced ceria ($CeO_{2-\delta}$) is capable of storing oxygen during lean-to-rich transition and thereby promoting the reduction of NO_x , while it is at the same time able to provide the oxygen necessary for CO and HC oxidation during rich-to-lean transition. [27, 35] The application of ceria in three-way catalytic converters is one of the well-established applications, but is far from being the sole one and many of the ceria applications mentioned in this work will soon find their way to larger commercial utilization.

4. Hydrothermally derived cerium(IV) oxide

Our group has been dealing with ceria for several years, focusing on the preparation of different ceria nanostruc-

tures, trying out different synthesis methods and different dopants for the enhancement of ceria properties. The most detailed research was conducted in the preparation of ceria nanoparticles prepared by hydrothermal synthesis and aimed for catalytic application, in the oxidation of volatile organic compounds. [14, 46, 49, 50]

Preliminary research included the doping of ceria with the same amount of various transition metals to enable the comparison of catalytic activity and overall influence of the dopant on the properties of ceria. [14] Doping with copper, manganese and zinc proved to be the most beneficial for the overall properties of ceria, resulting in spherical nanoparticles of very small sizes (~ 4 nm) and high specific surface areas (~ 200 m² g⁻¹), as well as very good catalytic activity as shown in Figure 9. Therefore, these metals were chosen for further research, and special emphasis was placed on copper and manganese. Ceria was doped with 10, 20, 30 and 40 mol. % of Cu, and 10, 20 and 30 mol. % of Mn.

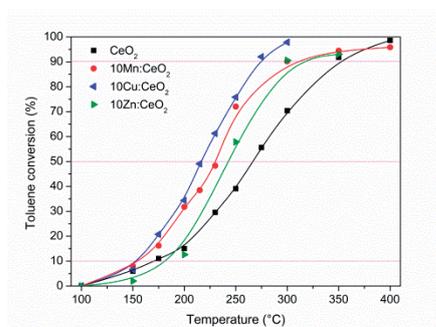


Figure 9. Preliminary catalytic activity results for pure and transition metal doped samples.

The as-prepared samples doped with manganese showed crystallite sizes around 4 nm, while those of samples doped with copper were around 3.3 nm, which is unprecedented for this synthesis method. Besides ceria, the manganese doped samples showed the presence of monoclinic sodium birnessite, $\text{Na}_{0.55}\text{Mn}_2\text{O}_4 \cdot 1.5 \text{H}_2\text{O}$, which consists of octahedral MnO6 sheets with Na ions and crystal H₂O molecules in the interlayer. [51] The said birnessite transforms into romanechite-like sodium manganese oxide, $\text{Na}_2\text{Mn}_5\text{O}_{10}$, upon thermal treatment at 500 °C. However, the presence of an additional phase does not have a negative effect on the properties of CeO₂. The specific surface area and thermal stability of the samples increases with the increase of the manganese amount. [50] The beneficial influence of manganese on the overall properties of ceria culminates in its catalytic activity. The catalytic activity of Mn doped samples in the process of toluene oxidation is significantly higher than that of pure ceria sample.

The copper doped samples exhibit no additional phases except ceria, which indicates that copper is incorporated into the CeO₂ crystal lattice forming a solid solution. All copper doped samples have better overall properties than pure ceria, in terms of thermal stability, higher amount of oxygen vacancies and lower band gap values, proving the doping advantageous. However, there is no drastic dif-

ference between the doped samples, with the exception being the 40 mol. % Cu doped ceria sample. This sample possesses the highest thermal stability, the highest number of oxygen vacancies as determined by XPS analysis, a distinct bimodal pore size distribution after thermal treatment at 500 °C which facilitates molecular transport and reduces diffusion limitations present in narrow uniform pores, and the lowest band gap value (2.71 eV) which is extremely favorable for photocatalytic applications. [52] These results are also reflected in the best catalytic activity of 40 mol. % Cu doped sample in the BTEX (benzene, toluene, ethylbenzene and o-xylene) oxidation process. [49]

The hydrothermal method proved to be a simple, yet efficient method for the preparation of pure and doped ceria samples of high purity, small crystallite sizes, excellent properties and very good catalytic activity in the oxidation of volatile organic compounds.

5. Conclusion

Cerium (IV) oxide is a material capable of a facile reversible redox process which enables the creation of oxygen vacancies, high oxygen mobility and oxygen storage capacity within the crystal lattice. This key feature of ceria allows its use in many different fields, while the introduction of nanostructural design and doping with metal ions of lower valence further enhance the overall advantageous properties of ceria and open up the possibility of creating new materials with improved properties.

6. Acknowledgements

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7. References

1. Borra, C.R., Vlught, T.J.H., Yang, Y., Offerman, S.E. Recovery of Cerium from Glass Polishing Waste: A Critical Review, *Metals* 8 (2018) 801.
2. Voncken, J.H.L. The Rare Earth Elements, Chapter 3: Physical and Chemical Properties of the Rare Earths, Springer International Publishing, 2016, pp. 53-72.
3. Dunnick, K.M., Morris, A.M., Badding, M.A., Barger, M., Stefaniak, A.B., Sabolsky, E.M., Leonard, S.S. Evaluation of the effect of valence state on cerium oxide nanoparticle toxicity following intratracheal instillation in rats, *Nanotoxicology* 10 (7) (2016) 992-1000.
4. Arenas, L.F., Ponce de León, C., Walsh, F.C. Electrochemical redox processes involving soluble cerium species, *Electrochim. Acta.* 205 (2016) 226-247.
5. Mogensen, M., Sammes, N.M., Tompsett, G.A. Physical, chemical and electrochemical properties of pure and doped ceria, *Solid State Ion.* 129 (2000) 63-94.

6. Sun, C., Li, H., Chen, L. Nanostructured ceria-based materials: synthesis, properties, and applications, *Energy Environ. Sci.* 5 (2012) 8475–8505.
7. Younis, A., Chu, D., Li, S. Chapter 3: Cerium Oxide Nanostructures and their Applications, in *Functionalized Nanomaterials*, Editor: M. A. Farrukh, IntechOpen, 2016, <http://dx.doi.org/10.5772/65937>.
8. Castleton, C.W.M., Lee, A.L. Description of polarons in ceria using Density Functional Theory, *J. Phys.: Conf. Ser.* 526 (2014) 012002, <https://doi.org/10.1088/1742-6596/526/1/012002>.
9. Shoko, E., Smith, M.F., McKenzie, R.H. A consistent picture of the charge distribution in reduced ceria phases, 2009, arXiv:0910.0669 [cond-mat.str-el].
10. Tan, J., Zhang, W., Lv, Y.H., Xia, A.L. Facile Preparation of Mn-doped CeO₂ submicrorods by composite-hydroxide-salt-mediated approach and their magnetic property, *Mat. Res.* 16 (2013) 689–694.
11. Kurajica, S., Munda, I.K., Brleković, F., Mužina, K., Dražić, G., Šipušić, J., Mihaljević, M. Manganese-doped ceria nanoparticles grain growth kinetics, *Journal of Solid State Chemistry*, 291 (2020) 121600.
12. Liu, L., Shi, J., Zhang, X., Liu, J. Flower-Like Mn-doped CeO₂ microstructures: synthesis, characterizations, and catalytic properties, *J. Chem.* 254750 (2015) 1–11.
13. Zhang, T., Kumar, E., Selvarajana, P., Muthuraj, D. Synthesis and characterization of CeO₂ nanocrystals by solvothermal route, *Mater. Res.* 16 (2013) 269–276.
14. Kurajica, S., Mužina, K., Dražić, G., Matijašić, G., Duplančić, M., Mandić, V., Župančić, M., Munda, I.K. A comparative study of hydrothermally derived Mn, Fe, Co, Ni, Cu and Zn doped ceria nanocatalysts, *Mater. Chem. Phys.* 244 (2020) 122689, <https://doi.org/10.1016/j.matchemphys.2020.122689>.
15. Tiwari, S., Rathore, G., Patra, N., Yadav, A.K., Bhattacharaya, D., Jah, S.N., Tseng, C.M., Liu, S.W., Biring, S., Sen, S. Oxygen and cerium defects mediated changes in structural, optical and photoluminescence properties of Ni substituted CeO₂, *J. Alloy. Comp.* 782 (2019) 689–698.
16. Kurajica, S., Lučić Blagojević, S. *Uvod u nanotehnologiju*, HDKI, Zagreb, 2017.
17. Lopez, J.M., Gilbank, A.L., Garcia, T., Solsona, B., Agouram, S., Torrente-Murciano, L. The prevalence of surface oxygen vacancies over the mobility of bulk oxygen in nanostructured ceria for the total toluene oxidation, *Appl. Catal., B*, 174–175 (2015) 403–412.
18. Tang, W.X., Gao, P.X. Nanostructured cerium oxide: preparation, characterization, and application in energy and environmental catalysis, *MRS Communications* 6 (2016) 311–329.
19. Sumi, H., Shimada, H., Yamaguchi, Y., Yamaguchi, T. Metal-supported microtubular solid oxide fuel cells with ceria-based electrolytes, *J. Ceram. Soc. Jpn.* 125 (4) (2017) 208–212.
20. Brown, E.C. *Electrochemically Deposited Ceria Structures for Advanced Solid Oxide Fuel Cells*, Doctoral thesis, California Institute of Technology, Pasadena, California, 2011.
21. Singhal, S.C. *Solid Oxide Fuel Cells*, *The Electrochemical Society Interface* 16 (4) Winter (2007) 41–44.
22. Singhal, S.C., Kendall, K. *High temperature solid oxide fuel cells: fundamentals, design and applications*, Elsevier, Oxford, 2003.
23. Pikalova, E.Yu., Bamburov, V.G., Murashkina, A.A., Neumin, A.D., Demin, A.K., Plaksin, S.V. *Solid Electrolytes Based on CeO₂ for Medium Temperature Electrochemical Devices*, *Elektrokhimiya* 47 (6) (2011) 738–744.
24. Pikalova, E.Yu., Kolchugin, A.A., Bamburov, V.G. Ceria-based materials for high-temperature electrochemistry applications, *Int. J. of Energy Prod. & Mgmt.* 1 (3) (2016) 272–283.
25. Kharton, V. V., Figueiredo, F.M., Navarro, L., Naumovich, E.N., Kovalesky, A.V., Yaremchenko, A.A., Viskup, A.P., Carneiro, A., Marques, F.M., Frade, J.R. Ceria-based materials for solid oxide fuel cells, *J. Mater. Sci.* 36 (2001) 1105–1117.
26. <https://www.cerespower.com/> (Access: 28.1.2020.)
27. Montini, T., Melchionna, M., Monai, M., Fornasiero, P. *Fundamentals and Catalytic Applications of CeO₂-Based Materials*, *Chem. Rev.* 116 (2016) 5987–6041.
28. Venancio, S.A., de Miranda, P.E.V. Synthesis of CeAlO₃/CeO₂-Al₂O₃ for use as a solid oxide fuel cell functional anode material, *Ceram. Int.* 37 (2011) 3139–3152.
29. Park, S., Vohs, J., Gorte, R. Direct Oxidation of Hydrocarbons in a Solid-Oxide Fuel Cell, *Nature* 404 (2000) 265–267.
30. Gorte, R.J., Vohs, J.M. Nanostructured Anodes for Solid Oxide Fuel Cells, *Curr. Opin. Colloid Interface Sci.* 14 (2009) 236–244.
31. Marina, O.A., Bagger, C., Primdahl, S., Mogensen, M. A Solid Oxide Fuel Cell with a Gadolinia-Doped Ceria Anode: Preparation and Performance, *Solid State Ion.* 123 (1999) 199–208.
32. Murray, E.P., Tsai, T., Barnett, S.A. A Direct-Methane Fuel Cell with a Ceria-Based Anode, *Nature* 400 (1999) 649–651.
33. Adijanto, L., Sampath, A., Yu, A.S., Cargnello, M., Fornasiero, P., Gorte, R.J., Vohs, J.M. Synthesis and Stability of Pd-CeO₂ Core-Shell Catalyst Films in Solid Oxide Fuel Cell Anodes, *ACS Catal.* 3 (2013) 1801–1809.
34. Sun, C., Xie, Z., Xia, C., Li, H., Chen, L. Investigations of Mesoporous CeO₂-Ru as a Reforming Catalyst Layer for Solid Oxide Fuel Cells, *Electrochem. Commun.* 8 (2006) 833–838.
35. Ramakrishnan, G., Naveen, K. Emission and dynamic characteristics of three way catalytic converter by computational fluid dynamics, *Int. J. Eng. Sci.* 6 (2016) 3503–3510.
36. Prakash, A.S., Shivakumara, S., Hegde, M.S. Single step preparation of CeO₂/CeAlO₃/g-Al₂O₃ by solution combustion method: Phase evolution, thermal stability and surface modification, *Mater. Sci. Eng. B* 139 (2007) 55–61.
37. Saravanan, T., Shanmugam, M., Anandan, P., Azhagurajan, M., Pazhanivel, K., Arivanandhan, M., Hayakawa, Y., Jayavel, R. Facile synthesis of graphene-CeO₂ nanocomposites with enhanced electrochemical properties for supercapacitors, *Dalton Trans.* 44 (2015) 9901–9908.
38. Dezfali, A.S., Ganjali, M.R., Naderi, H.R., Norouzi, P. A high performance supercapacitor based on a ceria/graphene nanocomposite synthesized by a facile sonochemical method, *RSC Adv.* 5 (2015) 46050–46058.

39. Lokhande, C.D., Dubal, D.P., Joo, O.S. Metal oxide thin film based supercapacitors, *Curr. Appl. Phys.* 11 (2011) 255-270.
 40. Chen, X., Paul, R., Dai, L. Carbon-based supercapacitors for efficient energy storage, *Natl. Sci. Rev.* 4 (3) (2017) 453-489.
 41. Shishesaz, M., Sarpoushi, M.R., Golozar, M.A. An Electrochemical Investigation of Nano Cerium Oxide/ Graphene as an Electrode Material for Supercapacitors, *Iranian Journal of Oil & Gas Science and Technology* 4 (1) (2015) 81-91.
 42. Ghosh, S., Thomas, T., Rao, G.R. Zr substitution aided enhancement of pseudocapacitive behavior of ceria, *Mater. Lett.* (2020), doi: <https://doi.org/10.1016/j.matlet.2020.127500>.
 43. Ren, Z., Peng, F., Li, J., Liang, X., Chen, B. Morphology-dependent properties of Cu/CeO₂ catalysts for the water-gas shift reaction, *Catalysts* 7 (2017) 48.
 44. Si, R., Raitano, J., Yi, N., Zhang, L., Chan, S., Flytzani-Stephanopoulos, M. Structure sensitivity of the low-temperature water-gas shift reaction on Cu-CeO₂ catalysts, *Catal. Today* 180 (2012) 68-80.
 45. Palmisano, P., Russo, N., Fino, D., Saracco, G., Specchia, V., Faraldi, P., Polverini, D., Artecioni, L. Doped ceria catalysts for an innovative self-cleaning domestic oven, 21st North American Catalysis Society Meeting 2009, *Proceedings* 1 (2009) 341-342.
 46. Duplančić, M., Kurajica, S., Tomašić, S., Minga, I. Catalytic oxidation of toluene on hydrothermally prepared ceria nanocrystals, *Chem. Biochem. Eng. Q.* 31 (2017) 375-383.
 47. Conesa, J.C., Martinez-Arias, A., Fernandez-Garcia, M., Soria, J. Surface Structure and Redox Chemistry of Ceria-Containing Automotive Catalytic Systems *Res. Chem. Intermed.*, 26 (2000) 103-111.
 48. Campbell, C.T., Peden, C.H.F. Chemistry - Oxygen Vacancies and Catalysis on Ceria Surfaces. *Science*, 309 (2005) 713-714.
 49. Mužina, K., Kurajica, S., Guggenberger, P., Duplančić, M., Dražić, G. Catalytic activity and properties of copper-doped ceria nanocatalyst for VOCs oxidation, *J. Mater. Res.* 37 (2022) 1929-1940.
 50. Kurajica, S., Ivković, I.K., Dražić, G., Shvalya, V., Duplančić, M., Matijašić, G., Cvelbar, U., Mužina, K. Phase composition, morphology, properties and improved catalytic activity of hydrothermally-derived manganese-doped ceria nanoparticles, *Nanotechnology* 33 (13) (2022) 135709.
 51. Kurajica, S., Munda, I.K., Dražić, G., Mandić, V., Mužina, K., Bauer, L., Matijašić, G. Manganese-doped, hydrothermally-derived ceria: The occurrence of birnessite and the distribution of manganese, *Ceram. Int.* 46 (18) (2020) 29451-29458.
 52. Mužina, K., Kurajica, S., Dražić, G., Guggenberger, P., Matijašić, G. True doping levels in hydrothermally derived copper-doped ceria, *J. Nanopart. Res.* 23 (2021) 149. 57
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