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CEO_2 -BASED MATERIALS FOR ENERGY SECTOR APPLICATIONS

CeO_2 -based materials have recently received great attention for the application in the energy sector due to their high oxygen ion mobility. This review highlights how these materials could improve the processes involved in the H_2 production and purification and the performances of Solid Oxide Fuel Cells (SOFC).

In the last decades, the continuous increase in the world population resulted in a considerable increase of the energy requirement. Today, the need of energy is filled mainly using fossil fuels (oil, natural gas, carbon), that will, soon or late, be used up and it could be related to the enhancement of air pollution and greenhouse gas emissions. For the future, the progress of the human society will need the development of sustainable technologies to fulfil the energy requirements.

The extensive use of renewable sources represents the first important aspect of the energy production for the future. Besides the well known hydroelectric and wind technologies, solar energy utilization

requires the development of more efficient materials for photon utilization in order to reach an extensive diffusion [1]. More reliable in the short-medium terms is the use of biomasses (when not used as food) as renewable sources for the production of fuels and chemicals [2, 3]. The search for efficient catalytic processes to convert non-edible biomasses (such as non-eatable oils, agricultural residues etc.) into chemicals (including H_2) and/or fuels is a must in the developing of the new biorefineries. On the other hand, the efficiency of the conversion of fuels into energy must be increased, with the development of more efficient processes and/or apparatus. In this context, fuel cells represent a promising technology since they can reach very high

conversion efficiency of the chemical energy of fuels into electricity. CeO₂-based materials may have a lot of applications in the transition to an environmental sustainable economy. Three Way Catalysts (TWCs), the apparatus able to remove the pollutant gases emitted by combustion engines, represent the most diffused application of CeO₂-ZrO₂ mixed oxides [4]. They allow to extend the operating conditions of the catalyst reaching very high efficiency in the pollutant abatement. Many other applications are reported for CeO₂-based materials, as heterogeneous catalysts [5], polishing materials [6], optical filters [7] or free radical scavengers [8].

In this review, the most important application of CeO₂-based materials in the energy sector are summarized. Starting from the crystal structure and its redox chemistry and transport properties, significant examples of the applications of CeO₂-based materials in the heterogeneous catalysts for H₂ production and purification and its role in the improvement of the performances of Solid Oxide Fuel Cells (SOFC) are highlighted. The examples reported in this review are not comprehensive of all the papers reported in the literature, but they have been chosen to represent the potentiality of CeO₂-based materials in the energy production.

Characteristics of CeO₂ and related materials

CeO₂ crystallizes in the fluorite structure, has a face-centred cubic unit cell (f.c.c.) with a space group Fm3m (a = 0.541134 nm, JCPDS 34-0394). In this structure, each cerium cation is coordinated by eight equivalent nearest-neighbour oxygen anions at the corner of a cube, each anion being tetrahedrally coordinated by four cations. The cubic structure is usually maintained also in doped materials forming solid solutions, such as Ce_{1-x}M_xO_{2-d}, where M is a metal dopant present in relatively small amount. CeO₂ is able to accommodate different extent of the doping cations depending on the ionic radius and the oxidation state of Mⁿ⁺ [9]. Following the empirical formulae reported by Kim [9], a critical radius (r_c) for the dopant cation can be calculated to minimize the elastic energy introduced in the CeO₂ lattice (r_c = 0.1106 nm for divalent cations and 0.1038 nm for trivalent cations). The experimental literature shows that CeO₂ fluorite structure is in fact very tolerant to dissolution of lower valent metal oxides with cation radii close to r_c to high concentration (above 40%) in some cases [10]. Above the solubility limit, the change of the crystal structure (forming a material with lower symmetry) or the segregation of a secondary phase can occur.

Many types of defects can be present in CeO₂-based materials. The most relevant for the applications in catalysis and in the material science are oxygen vacancies and small polarons.

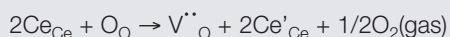
An oxygen vacancy is formed when an oxygen ion is missing in the crystal lattice or on the surface. Oxygen vacancies may be introduced in CeO₂ lattice (without altering the oxidation state of cerium) by doping with oxides of metals with oxidation state lower than (IV), e.g. by dissolution of CaO or Gd₂O₃, that can be expressed, following the Kröger-Vink notation*, as:



where the main symbol represents the species considered (V for a vacancy), the subscript represents the crystallographic site that the species occupies and the apex represents the electric charge with respect to the normal charge the crystallographic site (• for a positive charge and for a negative charge).

Oxygen vacancies (V^{••}_O) are involved in the oxygen ions diffusion inside CeO₂-based materials, giving to these materials an appreciable ionic conductivity. The conductivity mechanism is attributed to the hopping of oxide ions to vicinal vacant sites. The motion of oxygen ions can take place on the surface of the grains (grain boundaries) and through the bulk of the grains. The total conductivity consists of a contribution from both the parts of the grains. Since the grain boundaries are often badly conducting, the fabrication of very dense samples (with very large crystallite and grain sizes) minimizes the contribution of the grain boundaries to the total conductivity of the materials.

On the other hand, a small polaron is a defect created when an electronic carrier (electron or electron hole) becomes trapped at a given site as a consequence of the displacement of adjacent atoms or ions in the crystal lattice. As a consequence of the ions displacement, the crystallographic site that hosts the electronic carrier results distorted. The entire defect, i.e. electron or electron hole plus distortion, migrates by a thermally activated hopping, leading to electronic conductivity through the material. Due to the ability of cerium to switch between two oxidation states (Ce(III) and Ce(IV)), small polarons can be easily introduced inside the CeO₂ lattice. In this case, the defect corresponds to the combination of a Ce(III) ion plus the distortion in the lattice induced by this cation. Nowadays, it is generally accepted that the medium-high temperature reduction of CeO₂ is accompanied by the formation of oxygen vacancies inside the crystal structure. Accordingly to the Kröger-Vink notation, the process of ceria reduction may be written as:



or, in the case it is reduced by a gas (like hydrogen), it is:



As a consequence, reduced CeO₂-based materials are mixed ionic and electronic conductors.

The reduction of CeO₂ is commonly accepted to proceed through a step-wise mechanism [12, 13] by activation of the reducing agent on the surface, the formation of surface oxygen vacancies, the desorption of the oxidized products and the diffusion of the vacancies to the bulk. The formation of oxygen vacancies on the surface of ceria has been studied using Scanning Tunneling Microscopy (STM) [14]. The images obtained with atomic resolution for the CeO₂ (111) surface after reduc-

*For a detailed description of the Kröger-Vink notation, please refer to [11].

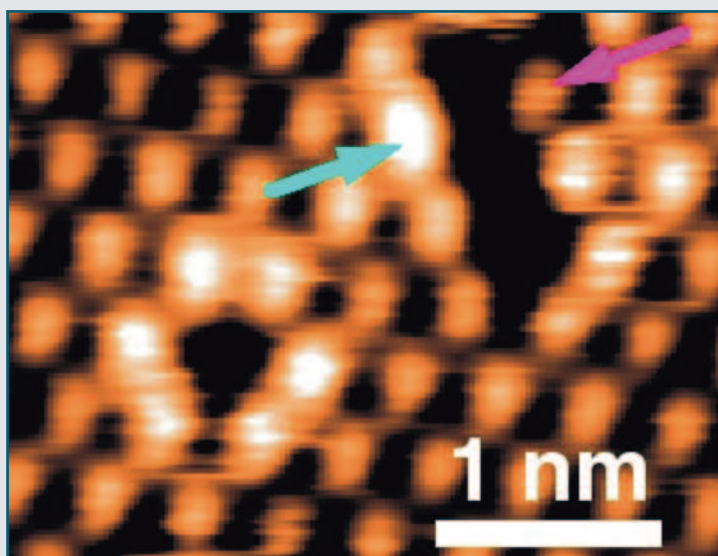


Fig. 1 - STM image of a single oxygen vacancy and a triple oxygen vacancies cluster. Arrows indicates the characteristic unit (2 surface + 1 sub-surface oxygen vacancies) present in all the vacancies clusters (adapted from [14], copyright 2005 Science AAAS)

tion in different extent revealed the population of the different types of oxygen vacancies. Simulations using the Density Functional Theory (DFT) allowed to identify the real atomic structure of each feature observed on the surface. The most important result of this study regards the structure of multiple oxygen vacancies. These type of defects are very important from a catalytic point of view because they are involved in the diffusion of oxygen inside the CeO_2 lattice and are the sites for the activation of various small molecules (O_2 , H_2O etc.). To obtain a good correspondence between the STM images and the DFT simulation, the presence of a sub-surface oxygen vacancy must be taken into account. Moreover, the DFT simulation revealed that the defects expose only reduced Ce(III) ions. Since no defects exposing oxidized Ce(IV) has been observed in the STM images, the study concluded that only the defects those expose only reduced cerium ions are stable (Fig. 1).

Traditional application of CeO_2 -based materials

The most diffuse and known application of CeO_2 -based materials is as promoter in the automotive Three-Way Catalysts (TWCs). Mounted after an internal combustion engine, their role is to remove the pollutant products of combustion of gasoline, such as carbon monoxide (CO), residual unburnt hydrocarbons (HC) and nitrogen oxides (NO_x). The oxidation reactions are promoted by Pt and Pd, while Rh is essential to catalyze the reduction of NO_x [15].

Fig. 2 presents the conversion efficiency of the three class of pollutants as a function of the air to fuel ratio (A/F). A good removal of all the pollutants is obtained only in a narrow windows around the stoichiometric value, which is near 14.6. This is achieved by a continuous control of the oxygen pressure in the gas stream and the modulation of the air and fuel flows by the electronic system of the car (the so called λ -sen-

sor). Nevertheless, the tight stoichiometry requirements are not easily attainable in a randomly (to the driving features) oscillating dynamic combustion and the gas phase coming out of the engine rapidly fluctuates between lean ($\text{A/F} > 14.6$) to rich conditions ($\text{A/F} < 14.6$) and viceversa.

The principal role of CeO_2 in TWCs is to act as oxygen buffer. Reduced ceria ($\text{CeO}_{2-\delta}$) is able to store oxygen during lean-to-rich transients, promoting the reduction of NO_x . On the other hand, CeO_2 is able to provide the oxygen needed for CO and HC oxidation during rich-to-lean transients. The maximum amount of oxygen that the $\text{CeO}_2/\text{CeO}_{2-\delta}$ system is able to provide/accept to/by the gas stream is called as Oxygen Storage Capacity (OSC).

Nowadays, the advanced TWCs available on cars contain CeO_2 - ZrO_2 solid solution [4]. The introduction of ZrO_2 into the CeO_2 lattice promotes the OSC of the material (enabling the catalyst to be active at lower temperature) and it stabilizes the surface area (reducing the deactivation by sintering).

CeO_2 -based materials for H_2 production

Hydrogen is asked to play an important role in the conversion of chemical industry towards a more and more increasing use of renewable sources. H_2 is fundamental for many important industrial processes, such as ammonia synthesis (~50%), cracking / refining processes (~40%), fuel purification from sulphur and nitrogen (HDS and HDN steps), methanol production (~8%), hydrogenation reactions, fuel production via Fischer-Tropsch synthesis [17]. In the energy sector, hydrogen is more properly conceived as an energy vector rather than an energy source as its production requires energy from other sources [18, 19]. Most of these applications requires highly pure H_2 .

Nowadays the search for more efficient, environmental friendly processes for H_2 production (through reforming processes) and purification (especially from CO) is an open field of many research groups worldwide. Fig. 3 shows a schematic representation of the various steps required to obtain syn-gas for dif-

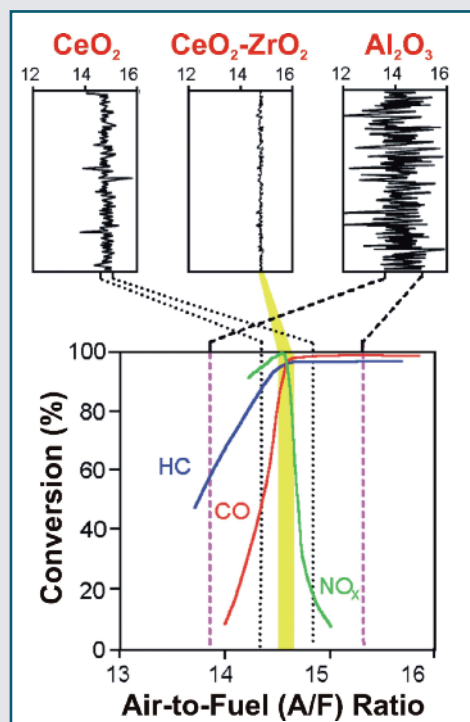


Fig. 2 - Conversion efficiency of HC, CO and NO_x , with the control of the Air-to-Fuel Ratio depending on different supports used in TWCs (adapted from [16], copyright 2000 Elsevier)

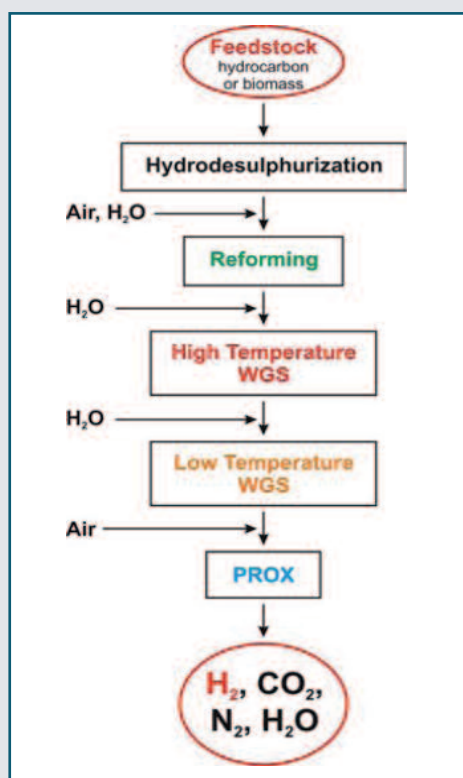


Fig. 3 - Schematic representation of the steps required for syn-gas production and H₂ purification

Syn-gas production through reforming processes

H₂ is extensively produced by purification of syn-gas, a mixture of H₂, CO and CO₂ (and by-products, such as CH₄) resulting from the reforming of carbonaceous compounds. The reaction usually proceeds at high temperature and catalysts are often used to increase conversion and selectivity. Syn-gas can be produced by the reforming of a large variety of feedstocks, including fossil fuels (methane, liquid or heavy hydrocarbons etc.) or renewable compounds (ethanol, glycerol, sugars etc.) [20, 21]. Since the current industrial hydrogen production is essentially based on fossil fuels, the implementation of new bio-refineries for the valorization of biomasses, especially those obtained from agriculture residues, is considered a successful alternative to the petrochemical plants for the sustainable preparation of chemicals (including H₂) and bio-fuels [22, 23].

The reforming process widely applied at industrial level is the steam reforming (SR). It is highly endothermic and it needs a high steam-to-carbon (S/C) ratio to prevent coke deposition on the catalysts. Some other processes are keeping great attention in recent years. In the dry reforming (DR) process, the feedstock reacts with CO₂ through an endothermic reaction and it presents the advantage to valorize this green-house gas using it as oxidizer. Partial oxidation (POX) is a mild exothermic process in which the feedstock reacts with a controlled amount of O₂ in order to form CO and H₂ instead of the products of complete oxidation (CO₂ and H₂O). In the auto-thermal reforming (ATR), the feedstock reacts with O₂ and H₂O in order to use the heat

ferent applications and/or to produce H₂ with high purity. The fuel is often purified by impurities, especially sulphur and nitrogen, and subjected to reforming by reaction with H₂O or O₂, or both, at high temperature. The H₂/CO ratio is then adjusted by the Water Gas Shift reaction (usually conducted in two steps at different temperatures). If high purity H₂ is needed, a further CO purification step is required. For fuel cells applications, the final purification is achieved by Preferential Oxidation (PROX) of the residual CO.

produced by POX to promote the SR; this process has the great advantage to be thermally neutral. Finally, the aqueous-phase reforming (APR) is a process working in the liquid phase at high pressure and low-medium temperature. It is particularly indicated in the reforming of non-volatile feedstocks obtained from biomasses [20, 21].

Reforming processes usually involve a rather complicated reaction networks. In general, a good reforming catalyst should be able to:

- efficiently activate the feedstock breaking the C-H, C-C and O-H bonds;
- avoid CO hydrogenation (to reduce the H₂ consumption by side reactions, such as hydrocarbon formation);
- avoid coke deposition (by polymerization or decomposition of intermediate species).

The reforming processes usually proceed on metal active phases, comprising metals of the Groups 8, 9 and 10 (Ni, Co, Ru, Pt, Pd, Rh, etc.) [20]. The role of the metallic component is, primarily, the activation of the feedstock's molecule by homolytic cleavage of C-H, C-C and O-H bonds with the formation of hydrogen and/or organic fragments adsorbed on metal particles. Further decomposition of these fragments on the metal surface results in the complete reforming of the feedstock. As a side reaction, fragment decomposition leads to carbon build-up and loss of activity.

CeO₂-based materials are often introduced in the formulation of the reforming catalysts as supports or promoters to increase the activity

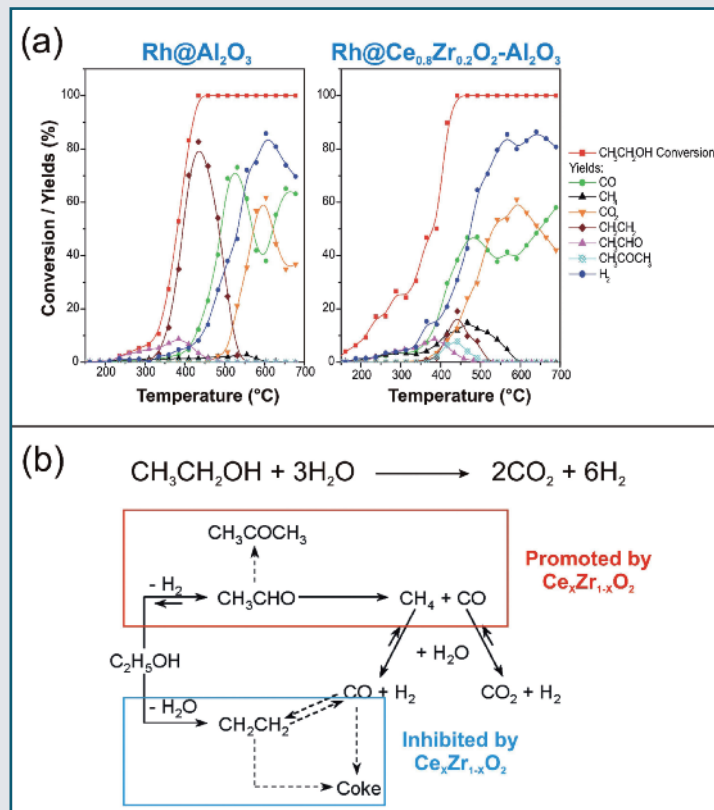


Fig. 4 - Effect of the Ce_xZr_{1-x}O₂ introduction in the formulation of nanostructured Rh@Ce_xZr_{1-x}O₂-Al₂O₃ catalysts for syngas production through ethanol steam reforming (adapted from [27], copyright 2007 Elsevier)

Tab. 1 - Use of CeO₂-based materials in reforming catalysts

Feedstock	Reforming process	Catalyst	Refs.
Methane	SR	Pd/CeO ₂ /Al ₂ O ₃	[28, 29]
	DR	Ni/CeO ₂ /Al ₂ O ₃	[30]
		Ru/Ce _{0.5} Zr _{0.5} O ₂	[26]
	POX	Rh/Ce _x Zr _{1-x} O ₂	[31]
		Pt/Ce _x Zr _{1-x} O ₂ /Al ₂ O ₃	[32]
		Ni/Ce _x Zr _{1-x} O ₂	[33]
	ATR	Ni/Ce _x Zr _{1-x} O ₂ /Al ₂ O ₃	[34]
		Pd/CeO ₂ /Al ₂ O ₃	[35]
Gasoline	POX	Ni/CeO ₂	[36]
	ATR	Rh/MgO/Ce _x Zr _{1-x} O ₂ monolith	[37]
Methanol	SR	Cu/CeO ₂ /Al ₂ O ₃	[38]
	ATR	ZnO-ZnCr ₂ O ₄ /Ce _x Zr _{1-x} O ₂	[39]
Ethanol	SR	Co/Ce _x Zr _{1-x} O ₂	[40]
		Rh/Ce _x Zr _{1-x} O ₂	[25]
		Ni/Ce _x Ti _{1-x} O ₂	[41]
		Rh@Ce _x Zr _{1-x} O ₂ -Al ₂ O ₃	[27]
	ATR	Rh/CeO ₂	[42]
		Cu/CeO ₂ /Al ₂ O ₃	[43]
Glycerol	SR	Ni/CeO ₂	[44]
		Ni/CeO ₂ /Al ₂ O ₃	[45]
		Pt/Ce _x Zr _{1-x} O ₂	[46]
		Ir/CeO ₂	[47]
	ATR	Rh/CeO ₂	[48]
	APR	Ni/CeO ₂ /Al ₂ O ₃	[49]

SR: Steam Reforming; DR: Dry Reforming; POX: Partial Oxidation;
ATR: Auto-Thermal Reforming; APR: Aqueous-Phase Reforming

and the stability of the catalysts. The presence of CeO₂ in the formulation of the support increases the metal phase dispersion, resulting in a higher activity for reforming reactions [24]. The high mobility of surface and lattice oxygen ions of doped CeO₂ has important implications on the reactivity of the metal (nano)particles that constitute the active phase, modifying the selectivity of the reforming reactions. This is due essentially to the ability of CeO₂-based materials to provide active oxygen to the metal particles. In fact, oxygen atoms are able to migrate from the surface of the CeO₂-based component to the metal particle perimeter, resulting in highly reactive oxygen species. These species strongly favor the oxidation reactions promoted by the active metallic phases [25, 26]. Furthermore, the decomposition of fragments adsorbed on the metal surface, which leads to carbon buildup and loss of activity, can be prevented. In principle, the mobility of oxygen in the support lattice could be optimized taking into account the composition of the reaction mixture; this is in order to prevent both carbon buildup on the surface and a too rapid oxidation of the hydrocarbon fragments, which would lead to complete oxidation. The mobility of oxygen species of CeO₂-based materials has important implication also to prevent the deac-

tivation by sulphur poisoning, a key problem in the reforming of oil-derived hydrocarbons.

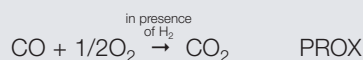
As an example, Fig. 4a presents the effect of the introduction of Ce_{0.8}Zr_{0.2}O₂ as promoter in the formulation of a nanostructured Rh-Al₂O₃ catalyst for ethanol steam reforming [27]. At high temperature (above 600 °C) both the systems produce syn-gas (H₂, CO and CO₂). The effect of the promoter is evident at intermediate temperatures. On the bare Rh-Al₂O₃, the reaction proceeds through dehydration to ethylene (promoted by the acid sites of the support) followed by reforming. When Ce_xZr_{1-x}O₂ is present, the reaction proceeds through the dehydrogenation to acetaldehyde followed by its decomposition and reforming. Fig. 4b presents the scheme of the reaction network involved in the steam reforming of ethanol. The effects of Ce_xZr_{1-x}O₂ on the different reactions is highlighted. Furthermore, the presence of Ce_xZr_{1-x}O₂ promoters result in a significant reduction of the amount of coke deposited on the catalysts after long term stability tests.

Tab. 1 summarizes some examples of reforming catalysts comprising a CeO₂-based component. This is not an exhaustive list of the works reported in the literature but it can give a representative picture of the importance of CeO₂-based materials, especially Ce_xZr_{1-x}O₂ solid solutions, as promoter in reforming processes.

H₂ purification through WGSR and PROX

After being produced, the H₂/CO ratio in the syn-gas must be adjusted to the desired value. From the industrial point of view, processes like Fischer-Tropsch synthesis, methanol synthesis or hydroformylation require well-defined H₂/CO/CO₂ ratios to be efficiently operative. On the other hand, H₂ used as energy vector in combination with PEM-FC must contain less than 10 ppm of CO, to avoid poisoning of the Pt-based anodes.

The most promising process to purify H₂ stream from CO appears to be a combination of the Water Gas Shift Reaction (WGSR) and the PReferential OXidation (PROX) of residual CO using O₂ [50]:



It is important to underline that the WGSR is an exothermic reaction ($\Delta H^\circ = -41$ kJ/mol) and the equilibrium constant decreases with increasing the temperature. So, to obtain a high CO removal, the operative temperature should be as low as possible and the CO concentration is dictated essentially by the thermodynamic of the reaction at the temperature of the exit of the reactor. As schematized in Fig. 3, the WGSR is usually performed in two consecutive stages: a high-temperature (HT-WGSR - operative between 300 and 450 °C) and a low temperature stage (LT-WGSR - operative between 200 and 300 °C). The HT-WGSR is commonly catalyzed by Fe₂O₃-Cr₂O₃ while the LT-WGSR usually involves Cu-ZnO catalysts. Moreover, the CO oxidation in the final PROX step requires the development of highly selective catalysts,

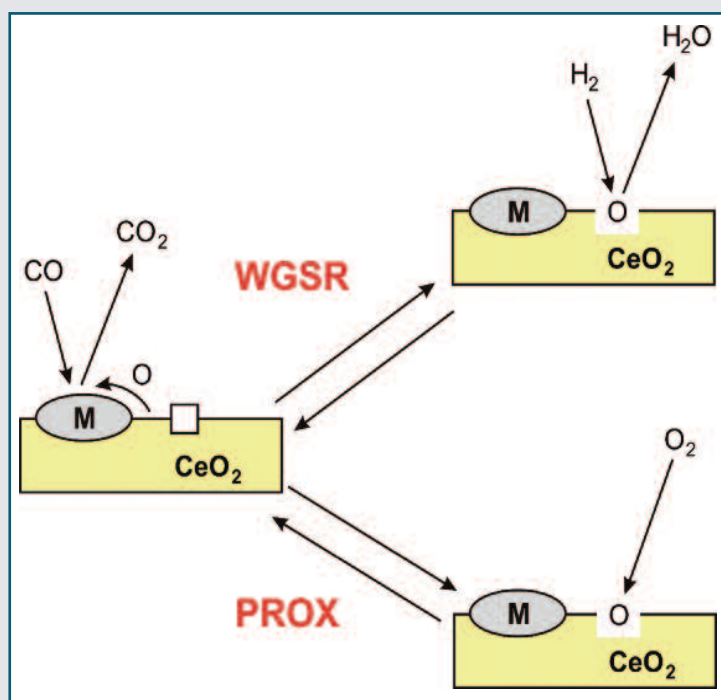


Fig. 5 - Schematic representation of the redox route involved in the WGSR and PROX processes

able to promote the removal of CO without a significant loss of H_2 . CeO_2 -based catalysts demonstrated promising performances in the H_2 purification technology, in particular for the processes operating at low temperature (LT-WGSR and PROX). Many noble and non-noble metals supported on CeO_2 (doped or not) revealed as active catalysts for H_2 purification. Among them, Pt, Au and Cu constitute certainly the most promising systems and therefore are the most studied in detail [51, 52]. Two reaction mechanisms have been proposed for CeO_2 -based catalysts under WGSR or PROX conditions:

- *the formate route*: the reaction involves the formation of OH groups on Ce ions, which react with CO to form formates. CO_2 and/or H_2 are produced by decomposition of the intermediate species (formates or carbonates adsorbed on the oxide surface). The role of the metal is to allow the adsorption of CO and to promote the cleavage of C-H bond of formate [53, 54];
- *the redox route*: reactive oxygen atoms are transferred from the support to the metal particles, leading to oxygen vacancies on the support surface. Active oxygen reacts with CO adsorbed on the metal particles producing CO_2 while H_2O or O_2 restore surface oxide anions, producing H_2 [55-59].

Recent experimental evidences suggest that the redox route is the predominant one, especially at the moderate temperatures involved in LT-WGSR and PROX processes (Fig. 5).

Among the noble metals, Au/ CeO_2 represents one of the most promising system studied for H_2 purification although many aspects have still to be clarified. In particular, the real form of Au particles (size and/or charge) under working conditions is still unclear. Au nanoparticles (less than 5 nm in size) [60] or cationic/partially positive gold

species ($Au^{δ+}$) [61-63] are candidates as active phase in Au/ CeO_2 catalysts. Despite the nature of the metal phase, the interaction of the metal nanoparticles with the CeO_2 surface represents a critical point to obtain active and selective catalysts. When metallic gold clusters are in intimate contact with the CeO_2 -based support, the Au atoms at the interface with the support would be expected to carry a small positive charge ($Au^{δ+}$) [63], providing the active sites for WGSR. On the other hand, the active sites for WGSR were reported as involving pure gold nanoparticles in contact with oxygen vacancies [64]. Moreover, the activity for WGSR was strongly related to the morphology at the nanoscale level, with different geometry and exposed crystal planes [65].

Very similar is the situation for Cu/ CeO_2 catalysts. Cu is usually present, in the as-prepared catalysts, as CuO entities. A strong interaction between CuO and oxygen vacancies, emphasized by an appropriate preparation route, is responsible for high activity under WGSR conditions [66]. Other authors proposed that metallic Cu interacting with oxygen vacancies on CeO_2 produces the active sites [67, 68]. Moreover, the activity of Cu/ CeO_2 catalysts can be incremented by doping of the support with ZrO_2 (which makes CeO_2 reduction easier and stabilizes the surface area of the support), confirming the importance of the redox properties of CeO_2 on the reaction rate [69]. Concerning PROX, a partial reduction of Cu(II) at the interface CuO- CeO_2 is observed and the CO conversion well fits the intensity of the Cu(I)-CO band of IR spectra [70, 71]. *In-situ* XAFS spectroscopy evidenced that partially reduced CuO entities are present when CO oxidation is predominant while, at higher temperature, fully reduction of CuO to Cu is responsible for H_2 oxidation [72].

Doped- CeO_2 in SOFC

Fuel cell technologies are expected to substantially reduce oil dependence and environmental impacts compared to conventional combustion-based power generation technologies. Solid Oxide Fuel Cells (SOFCs) represent a promising alternative for high-power applications such as for distributed auxiliary power units.

Fig. 6a presents the schematic representation of a SOFC. The electrolyte at the heart of each cell is a doped ceramic oxide with oxygen vacancies in his structure and it carries the charge between the half reactions at the cathode and the anode. The cathode (or air electrode) and the anode (or the fuel electrode) are the sites for each half reaction: oxygen is reduced to oxide ions consuming electrons at the cathode and fuel is oxidized forming electrons at the anode. SOFCs possess the advantages of high efficiency, ability to utilize high temperature exhaust from co-generation and the possibility of internal reforming, being fed directly with hydrocarbons. Nevertheless, high temperature is commonly required for SOFC's operation, resulting in long start up time and thermal stress of the constructing materials. CeO_2 -based materials can play an important role in the improvement of the performances of each component of SOFC, resulting in the decrease of the operative temperature.

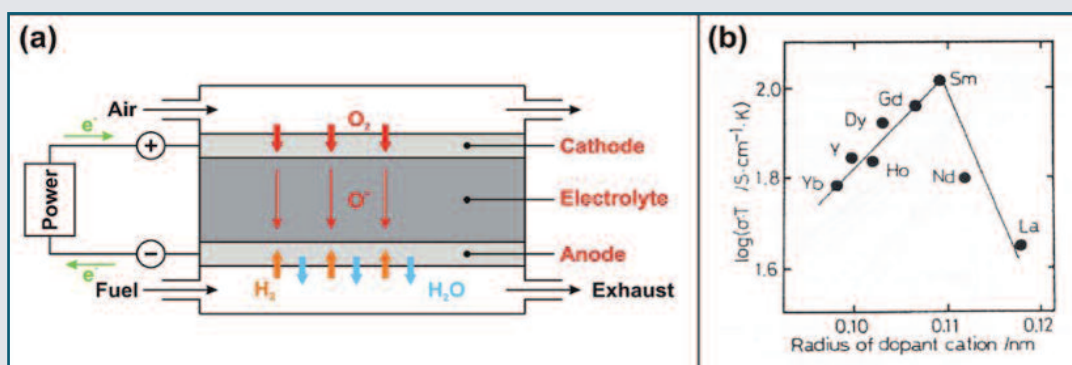


Fig. 6 - Part (a): Working outline of a Solid Oxide Fuel Cell (SOFC); Part (b): Effect of the ionic radius of trivalent lanthanides [Ln(III)] on the ionic conductivity of Ce_{0.8}Ln_{0.2}O_{1.9} electrolytes (reproduced from [73], copyright 1992 Elsevier)

Electrolytes

In a SOFC, the electrolyte must be ionically conductive and electronic insulating, in order to allow the transport of oxide ions from the cathode to the anode and to avoid the short circuit of the cell. The most used electrolyte is ZrO₂ doped with 3-8 mol% of Y₂O₃ (Yttria Stabilized Zirconia - YSZ). It is characterized by good chemical and mechanical stability with high quality available raw materials [74] and it possesses a pure ionic conductivity. For this reason, an acceptable conductivity through the electrolyte is obtained only operating at high temperature (800-1000 °C), conditions favouring the reaction with cathode's materials (usually La-based perovskites) forming undesired insulating phases (such as La₂Zr₂O₇).

As an alternative to ZrO₂-based materials, CeO₂-based electrolytes have high oxygen conductivity when doped with Gd₂O₃ (GDC), Sm₂O₃ (SDC), Y₂O₃ (YDC) and CaO (CDC). Eguchi *et al.* [73] reported that the ionic conductivity of lanthanide-doped ceria, such as (CeO₂)_{0.8}(LnO_{1.5})_{0.2} materials, depends on the ionic radius of the trivalent lanthanide dopant [Ln(III)] (from La to Yb), reaching a maximum for Sm(III) and Gd(III) (Fig. 6b). These are the ions with the best mismatch with the critical radius (r_c) obtained by the empirical formulae proposed by Kim [9]. Although these materials have been shown to be more stable than ZrO₂-based electrolytes, they become unstable under reducing conditions as well as above 700 °C due to increasing electronic conductivity that causes cell to short circuit. Consistently, CeO₂-based electrolytes represent the best choice for Intermediate Temperature SOFC (IT-SOFC), operating between 500 and 700 °C. In this temperature range, GDC presents a ionic conductivity which is almost one order of magnitude higher than that of YSZ [75].

Advanced Electrodes

The electrodes of a SOFC must have high ionic and electronic conductivity, an adequate porosity (to allow the diffusion of reagents and products), a good mechanical compatibility with the other parts of SOFC

and an extended Triple Phase Boundary (TPB). The TPB of an electrode is the contact area among the three phases necessary for electrochemical reactions at the electrode: ion conducting phase, electron conducting phase and gas phase. A good fuel cell maximizes the TPB area, allowing the reaction to occur in various sites, thus maximizing current flow. To fit this requirement, the electrodes are

composite systems as illustrated in Fig. 7a: an ionic conductor (usually the same material used for the electrolyte) and an electronic conductor are in intimate contact in order to maximize the number of sites for the electrochemical reaction with the gas phase. As a consequence on the increase TPB, the Area Specific Resistance (ASR) of the electrodes is strongly reduced. Fig. 7b shows an example of this result, presenting the differences in Nyquist plots obtained for symmetrical cells using a pure or a composite electrode for the cathodic O₂ reduction reaction.

The most studied materials for SOFC's cathodes, where O₂ is reduced to oxygen ions, are perovskites with general formula ABO_{3-δ} where A is usually La(III) partially substituted by Ca(II), Sr(II) or Ba(II) and B is a transition metal (such as Mn, Fe, Co, Ni or their

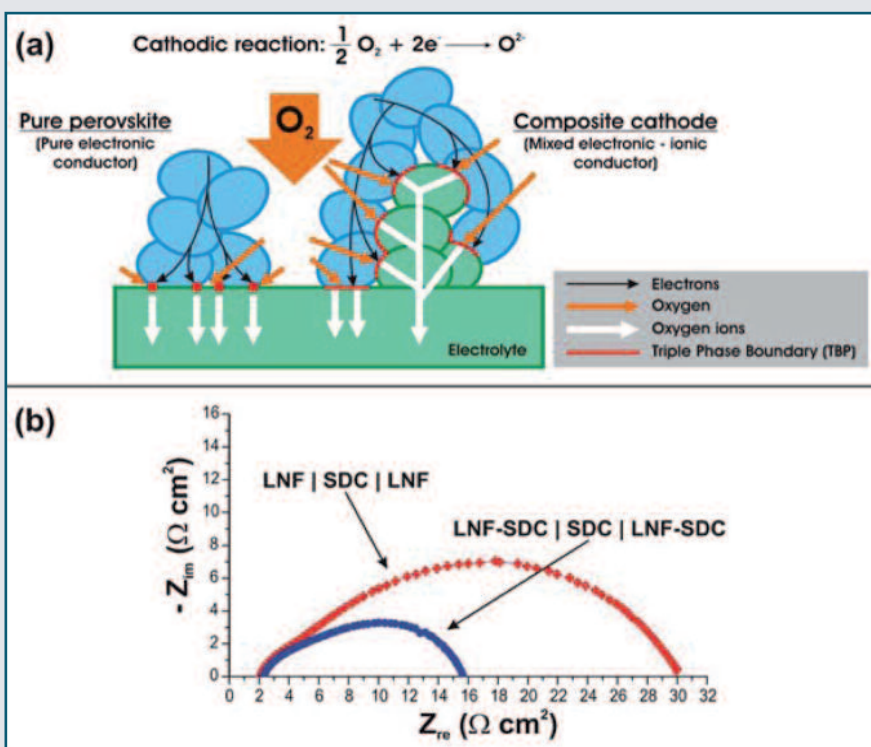


Fig. 7 - Part (a): Increase in the Triple Phase Boundary (TPB) by the use of a composite electrode; Part (b): Nyquist plot at 700 °C for symmetric cells using Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) as electrolyte and pure LaNi_{0.6}Fe_{0.4}O₃ (LNF) and composite LaNi_{0.6}Fe_{0.4}O₃-Ce_{0.8}Sm_{0.2}O_{1.9} (LNF-SDC) cathodes (adapted from [76], copyright 2007 American Chemical Society)

combination) [75]. These materials are Mixed Ionic-Electronic Conductors (MIEC), although usually a rather low ionic conductivity is observed [77, 78]. To extend the TPB in order to increase the performances of the SOFC, a composite cathode must be used. Unfortunately, La-based perovskites may react with YSZ forming insulating phases, such as $\text{La}_2\text{Zr}_2\text{O}_7$. To avoid these undesired reactions, the use of ZrO_2 -based electrolytes should be avoided or low temperature processing technologies must be employed [79]. In this case, the low temperature adopted will result in a lower conductivity of the cathode.

The interaction of doped ceria with cathode materials (perovskites) is lower than that of zirconia: Ce(IV) , which is larger than Zr(IV) , cannot replace Zr into the zirconate structure, avoiding the formation of insulating materials at the interface between the electrolyte and the cathode. GDC and SDC are most commonly used since do not react with a variety of La-based perovskites to give secondary materials ([80] and reference therein). Moreover, ceria-based interlayers are often applied between YSZ electrolyte and the cathode to prevent the undesired reactions ([80] and reference therein).

SOFCs' anodes, where the fuel is oxidized and the electrons are released to the external circuit, are usually made by a ceramic-metal composite (a so called *cermet* material). Due to its low cost and processing ease, the most used cermet is a combination of Ni and YSZ, providing for the electronic and ionic conductivity respectively. Since NiO has a low solubility into YSZ, NiO-YSZ composite can be sintered at high temperature maintaining, at the same time, a sufficient porosity to allow the gas diffusion. After *in-situ* reduction, the Ni-YSZ cermet is obtained. For the cermets where components have similar grain size, the best performances can be obtained with 30vol% of Ni while a substantial scatter is always observed due to microstructural differences [81]. The introduction of CeO_2 -based additives and layers is widely considered among the most promising direction in the development of advanced anodes. The advantages are related to a very high catalytic activity of ceria in the oxidation reactions involving oxygen, in particular to carbon oxidation beneficial for the fuel cells operating with hydrocarbons and bio-gas. Moreover, Ni- CeO_2 and Cu- CeO_2 cermets can be easily fabricated and operate with good performances with humidified H_2 , CO or syn-gas [82,83]. Moreover, they may operate internal reforming or direct oxidation of the fuel,

with the SOFC fed directly with hydrocarbons [83-88] or alcohols [89, 90]. Finally, doped CeO_2 further improves the performances of SOFCs' anodes [91-93] and increase the sulphur tolerance of the anode [94].

Conclusions

The peculiar characteristics of CeO_2 -based materials, such as the high oxygen ions mobility, allow for their extensive application in the energy sector. In this context, particularly relevant is their use as catalyst promoters in many reactions of production (reforming processes) and purification (Water Gas Shift and Preferential Oxidation) of hydrogen. Moreover, doped CeO_2 is a fundamental component for reducing the operative temperature of Solid Oxide Fuel Cells. It increases the Triple Phase Boundary on the cathodic side and promotes the oxidation/reforming reaction on the anodic site. After the extensive use of CeO_2 - ZrO_2 in the Three Way Catalysts, in the next decades we could assist to a new widespread diffusion of CeO_2 -based materials.

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References

- [1] E. Serrano *et al.*, *Renew. Sust. Energ. Rev.*, 2009, **13**, 2373.
- [2] A. Sivasamy *et al.*, *ChemSusChem*, 2009, **2**, 278.
- [3] J.N. Chheda *et al.*, *Angew. Chem. Int. Edit.*, 2007, **46**, 7164.
- [4] J. Kaspar *et al.*, *Catal. Today*, 1999, **50**, 285.
- [5] A. Trovarelli *et al.*, *Catal. Today*, 1999, **50**, 353.
- [6] X. Feng *et al.*, *Science*, 2006, **312**, 1504.
- [7] S. Yabe, T. Sato, *J. Solid State Chem.*, 2003, **171**, 7.
- [8] Y.Y. Tsai *et al.*, *Nanomedicine*, 2008, **3**, 637.
- [9] D.J. Kim, *J. Amer. Ceram. Soc.*, 1989, **72**, 1415.
- [10] T.H. Etsell, S.N. Flengas, *Chem. Rev.*, 1970, **70**, 339.
- [11] F.A. Kröger, H.J. Vink, in *Solid State Physics*, vol. 3, F. Seitz, D. Turnbull (Eds.), 1956, 273.
- [12] J. El Fallah *et al.*, *J. Phys. Chem.*, 1994, **98**, 5522.
- [13] S. Bernal *et al.*, *J. Phys. Chem.*, 1995, **99**, 11794.
- [14] F. Esch *et al.*, *Science*, 2005, **309**, 752.
- [15] J. Kaspar *et al.*, *Catal. Today*, 2003, **77**, 419.

- [16] M. Shelef, R.W. McCabe, *Catal. Today*, 2000, **62**, 35.
- [17] R. Ramachandran, R.K. Menon, *Int. Hydrogen Energ.*, 1998, **23**, 593.
- [18] S. Adhikari et al., *Int. J. Hydrogen Energ.*, 2007, **32**, 2875.
- [19] N. Luo et al., *Energ. Fuels*, 2007, **21**, 3505.
- [20] R.M. Navarro et al., *Chem. Rev.*, 2007, **107**, 3952.
- [21] J.D. Holladay et al., *Catal. Today*, 2009, **139**, 244.
- [22] S. Fernando et al., *Energ. Fuels*, 2006, **20**, 1727.
- [23] M. Kleinert, T. Barth, *Energ. Fuels*, 2008, **22**, 1371.
- [24] R. Craciun et al., *Appl. Catal. A-General*, 2002, **230**, 153.
- [25] H.S. Roh et al., *Top. Catal.*, 2008, **49**, 32.
- [26] S. Menad et al., *Catal. Lett.*, 2003, **89**, 63.
- [27] T. Montini et al., *Appl. Catal. B-Environmental*, 2007, **71**, 125.
- [28] W.H. Cassinelli et al., *Catal. Lett.*, 2008, **120**, 86.
- [29] L.S.F. Feio et al., *Appl. Catal. A-General*, 2007, **316**, 107.
- [30] N. Laosiripojana et al., *Chem. Eng. J.*, 2005, **112**, 13.
- [31] S. Eriksson et al., *Appl. Catal. A-General*, 2007, **326**, 8.
- [32] F.A. Silva et al., *Appl. Catal. A-General*, 2008, **335**, 145.
- [33] S. Xu, X.L. Wang, *Fuel*, 2005, **84**, 563.
- [34] J.C. Escritori et al., *Catal. Commun.*, 2009, **10**, 1090.
- [35] L.S.F. Feio et al., *Appl. Catal. A-General*, 2008, **348**, 183.
- [36] H.H. Ibrahim, R.O. Idem, *Chem. Eng. Sci.*, 2007, **62**, 6582.
- [37] A. Qi et al., *Int. J. Hydrogen Energ.*, 2007, **32**, 981.
- [38] X.R. Zhang, P.F. Shi, *J. Mol. Catal. A-Chem.*, 2003, **194**, 99.
- [39] N. Liu et al., *Fuel Process. Technol.*, 2008, **89**, 574.
- [40] S.S.Y. Lin et al., *Appl. Catal. A-General*, 2009, **366**, 252.
- [41] J.L. Ye et al., *Int. J. Hydrogen Energ.*, 2008, **33**, 6602.
- [42] W. Cai et al., *Catal. Today*, 2008, **138**, 152.
- [43] M. Turco et al., *Appl. Catal. B-Environmental*, 2009, **91**, 101.
- [44] S. Adhikari et al., *Energ. Fuels*, 2008, **22**, 1220.
- [45] L.P.R. Profeti et al., *Int. J. Hydrogen Energ.*, 2009, **34**, 5049.
- [46] R.R. Soares et al., *Angew. Chem. Int. Edit.*, 2006, **45**, 3982.
- [47] B. Zhang et al., *Int. J. Hydrogen Energ.*, 2007, **32**, 2367.
- [48] D.C. Rennard et al., *ChemSusChem*, 2009, **2**, 89.
- [49] A. Iriondo et al., *Top. Catal.*, 2008, **49**, 46.
- [50] D.L. Trimm, *Appl. Catal. A-General*, 2005, **296**, 1.
- [51] C. Ratnasamy, J. Wagner, *Catal. Rev.*, 2009, **51**, 325.
- [52] N. Bion et al., *Top. Catal.*, 2008, **51**, 76.
- [53] T. Shido, Y. Iwasawa, *J. Catal.*, 1993, **141**, 71.
- [54] T. Shido, Y. Iwasawa, *J. Catal.*, 1992, **136**, 493.
- [55] G.S. Zafiris, R.J. Gorte, *J. Catal.*, 1993, **139**, 561.
- [56] G.S. Zafiris, R.J. Gorte, *J. Catal.*, 1993, **143**, 86.
- [57] T. Bunluesin et al., *Appl. Catal. B-Environmental*, 1998, **15**, 107.
- [58] K. Li et al., *Appl. Catal. B-Environmental*, 2000, **27**, 179.
- [59] A. Wootsch et al., *J. Catal.*, 2004, **225**, 259.
- [60] N. Hickey et al., *Chem. Mater.*, 2007, **19**, 650.
- [61] Q. Fu et al., *Science*, 2003, **301**, 935.
- [62] M.F. Camellone, S. Fabris, *J. Am. Chem. Soc.*, 2009, **131**, 10473.
- [63] D. Tibiletti et al., *J. Phys. Chem. B*, 2005, **109**, 22553.
- [64] J.A. Rodriguez et al., *Top. Catal.*, 2007, **44**, 73.
- [65] R. Si, M. Flytzani-Stephanopoulos, *Angew. Chem. Int. Edit.*, 2008, **47**, 2884.
- [66] L. Li et al., *Catal. Lett.*, 2009, **130**, 532.
- [67] X. Wang et al., *J. Phys. Chem. B*, 2006, **110**, 428.
- [68] J.A. Rodriguez et al., *Catal. Today*, 2009, **143**, 45.
- [69] S. Pradhan et al., *Catal. Today*, 2009, **141**, 72.
- [70] D. Gamarra et al., *J. Am. Chem. Soc.*, 2007, **129**, 12064.
- [71] D. Gamarra et al., *J. Phys. Chem. C*, 2007, **111**, 11026.
- [72] A. Martinez-Arias et al., *Top. Catal.*, 2009, **52**, 1425.
- [73] K. Eguchi et al., *Solid State Ionics*, 1992, **52**, 165.
- [74] E. Ivers-Tiffée et al., *J. Eur. Ceram. Soc.*, 2001, **21**, 1805.
- [75] K.C. Wincewicz, J.S. Cooper, *J. Power Sources*, 2005, **140**, 280.
- [76] M. Bevilacqua et al., *Chem. Mater.*, 2007, **19**, 5926.
- [77] A. Esquirol et al., *J. Electrochem. Soc.*, 2004, **151**, A1847-A1855.
- [78] K.J. Yoon et al., *J. Electrochem. Soc.*, 2009, **156**.
- [79] Y. Huang et al., *Electrochem. Solid St. Lett.*, 2006, **9**, A237-A240.
- [80] J.W. Fergus, *J. Power Sources*, 2006, **162**, 30.
- [81] E.V. Tsipis, V.V. Kharton, *J. Solid State Electr.*, 2008, **12**, 1367.
- [82] O. Costa-Nunes et al., *J. Power Sources*, 2005, **141**, 241.
- [83] H.P. He et al., *J. Electrochem. Soc.*, 2003, **150**, A1470-A1475.
- [84] S. An et al., *State Ionics*, 2004, **175**, 135.
- [85] W. Wang et al., *J. Power Sources*, 2006, **159**, 68.
- [86] C. Lu et al., *Solid State Ionics*, 2002, **152-153**, 393.
- [87] M. Lo Faro et al., *J. Appl. Electrochem.*, 2007, **37**, 203.
- [88] A. Sin et al., *J. Power Sources*, 2007, **164**, 300.
- [89] M. Cimenti, J.M. Hill, *J. Power Sources*, 2010, **195**, 54.
- [90] X.F. Ye et al., *Electr. Commun.*, 2009, **11**, 823.
- [91] K.Y. Ahn et al., *Electrochem. Solid St. Lett.*, 2005, **8**, A414-A417.
- [92] A. Hornes et al., *J. Power Sources*, 2009, **192**, 70.
- [93] C. Lu et al., *J. Electrochem. Soc.*, 2003, **150**, A354-A358.
- [94] H.P. He et al., *Electrochem. Solid St. Lett.*, 2005, **8**, A279-A280.

RIASSUNTO

Materiali a base di CeO₂ per applicazioni nel settore energetico

Le peculiari caratteristiche di CeO₂, quale l'elevata mobilità degli ioni ossido, consente una sua ampia applicazione nel settore energetico. CeO₂ trova applicazione quale promotore nei catalizzatori impiegati nei processi di produzione (attraverso reforming) e nella purificazione di H₂ (conversione del gas d'acqua ed ossidazione preferenziale). CeO₂ drogata è inoltre un componente chiave di celle a combustibile ad ossidi solidi, consentendo un significativo abbassamento della loro temperatura operativa.