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Advanced (electro) ceramics and innovative energy technologies

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Abstract

The principal drivers of the new direction of research in energy technologies can be exemplified in three major targets: security of supply, environmental pollution issues (with particular reference to the Kyoto protocol), and adherence to the new European legislation related to the deregulation of the energy market. All these drivers contribute to the introduction of new technologies that better fit the requirements of the new scenario in which all the actors in the energy field are working. In this view, the contribution of Advanced Ceramics to such a big effort, with the identification of some development routes needed in terms of new materials and technologies, is analysed. In particular, the possible future trends in Solid Oxide and High Temperature PEM fuel cells, as well as oxygen and hydrogen pumping for hydrogen production connected with R&D in Advanced Ceramics, are discussed.

1. Introduction

Economic and environmental factors are pushing dramatic changes on the energy production and distribution market. The principal drivers of this incoming revolution can be summarized in three principal elements: (i) unpredictability of supply and strong dependence on politically unstable countries; (ii) environmental and global warming issues, that in the Kyoto Protocol received official recognition; (iii) the concomitant new policy of liberalisation of the energy market with the consequent effect on the volatility of the energy business.

As a consequence of this, governments must recognize the strict link between energy and environment and are forced to put innovative solutions into effective strategies to balance energy, economic growth and national security priorities with environmental and public health demands.

1.1. Security of supply

The future depletion of global energy resources imposes a new long-term strategy, realizing a smooth day-to-day operation of the power and fuel supply system is no longer practicable. For example, the EU is predicted to be dependent by 2020 for 75% of its gas supply and for 83% of oil supply.[1] New energy technologies can contribute to security of supply objectives in several ways, by reducing fuel demand through end-use energy efficiency measures, by enabling the use of diversified fuel sources, e.g. enabling fuel switching, fuel flexibility and by utilizing renewable energy sources. However, only major efforts in R&D will be able to make competitive such new technologies in a market subjected to revolutionary changes even in the short to medium term.

1.2. Pollution

Around 94% of CO_2 emissions in Europe are attributable to the energy sector as a whole; oil consumption accounts for 50% of CO_2 emissions in EU, natural gas for 22% and coal for 28%. In terms of consumer sectors, electricity generation is responsible for 37% of CO_2 emissions, transport for 28%, households for 14%, industry for 16% and the services sector for 5%. Some 90% of the projected growth in CO_2 emissions will be from the transport sector. According to the EU Commission, to stabilise the CO_2 concentration at the current level, emissions would have to be cut by 50–70% immediately.[1] In this view, the commitments of the

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Kyoto Protocol can only be a first step towards a complete solution of the greenhouse gas emissions problem, and greater and more ambitious long term objectives are necessary. Stabilizing and reducing greenhouse gas emissions require fearless and often innovative policy choices aimed at increasing energy efficiency and conservation and fuel switching that will meet resistance from powerful economic and political interests.

1.3. Deregulation

This is an international trend and could contribute to the volatility in the energy market. Until now in the EU countries electricity and gas generation, transmission and distribution were dominated by monopolies. Consumers inevitably had no choice and no guarantee of service standards, and the final cost was not a limiting factor for the energy companies in the choice of type of technologies, primary fuels and systems. Privatization legislation is encouraging real competition and the larger companies will create new policy to better address global competition and satisfy local needs. The concomitant trend in the confluence of production, distribution and service in the electricity and gas network will give unprecedented choice and flexibility to consumers. In this new scenario new technical solutions will play a significant role, addressing at the same time the requirements of new actors in the energy market, that need low investment costs and short pay-back time, and customers who will have a lower electricity and heat costs with a more efficient and simplified personalized service.

2. Technical trends

The scenario described above constitutes the background for the current trends of R&D in the energy sector, that implies, as main strategic and technological consequences, a widely distributed energy network, a strong increase in fuel flexibility, especially for transport purposes, and a full exploitation of emerging, highly efficient energy technologies.

2.1. Distributed energy

Several advantages are thought to come from a close location of the generation site to the load; a reduced cost of electricity will derive for the consumer and new profits for the utilities will likely arise from a stronger customer relationship, resulting in a full energy service. Smaller and modular plants will also require shorter construction time and offer faster investment pay-back; this, in turn, will also encourage new operators to enter a less risky market.

In the light of the above, the introduction of new technologies appears to be favored, in this revolutionary energy scenario, with respect to a possible adaptation of the traditional ones.

2.2. Fuel flexibility

A first step is currently being carried out, as new gasoline and diesel formulations can find application in advanced ICEs, with considerable advantages in terms of efficiency and pollution; the hydrocarbon industry, as well as the car-makers push towards such solutions, since these do not pose problems in terms of infrastructure or on-board storage. Natural gas, optimal for stationary applications, is also a candidate for massive automotive use although, from the viewpoint of the security of supply, some dependency cannot be ruled out. On the other hand, if we want to face the above cited drivers, fuels derived from renewable resources, i.e. alcohols and hydrogen, have to be primarily considered, especially for the automotive applications. Technical, socio-economic and political factors will all together play important roles in the timing and level of introduction of such fuels in the market.

3. New technologies and fuel cells

Fuel cells (FC) are the principal candidates to replace the traditional ways to transforming, producing and storing energy, due to their exceptional flexibility in applications as centralised or distributed stationary plants, in automotive, as well as their capability of integration with different energy sources (including renewables) and technologies as (micro)turbines and heat pumps. Only on the basis of their recognised characteristics, such as high overall efficiency, friendly environmental impact and propensity to cogeneration, do FCs appear to be the proper technology to answer the many different demands of the future energy market and fit the often conflicting viewpoints of producers and customers.

Advanced ceramics are key constituents of these electrochemical devices, with particular respect to Solid Oxide Fuel Cells, based on ionic oxygen electrolytes. This type of FC is characterised by the high (700–1000 °C) working temperature that makes it particularly suitable for stationary power plants where the high quality heat produced can also be advantageously used. Relevant spin-offs of this technology, directly derived from the R&D of oxygen electrolytes, are the oxygen pumps, that produce pure oxygen from air, and the Catalytic Membrane Reactors (CMR) that allow a more efficient and cost-effective separation of hydrogen from syngas with respect to the traditional gas–solid steam reforming reactor.

The most recent R&D activities on inorganic proton conductors will likely open the way to a new FC technology with unique features, since the operating temperature at which the electrolyte displays its conductivity is between 300 and 500 °C, a range not currently covered by other FCs. The activity in this field is continuously increasing and the most recent results, coming from different labs, promise a rapid development in the near future. Strictly correlated with this research area, current investigations on mixed (electronic–ionic) conductors for oxygen and hydrogen separation could be relevant for a number of energy technologies of the wished "hydrogen economy".

3.1. Solid oxide fuel cells (SOFC)

Solid oxide fuel cells, currently working between 800–1000 °C, are the favoured candidates for stationary applications in the distributed energy scenario, both in "micropower on site" configuration (<1 MW) and in multi-MW power stations, due to the good fuel flexibility and the very high electrical performance, if in combination with microturbines. Table 1 lists some of the projects currently under development for SOFC commercialisation. The techno-economic potential of this technology, however, has at present to face two main critical issues, i.e. the development of a low cost production process for the cell components and their still insufficient durability. As for this latter aspect, in fact, the most investigated and used in practice, yttria-stabilized zirconia electrolyte displays high conductivity at temperatures around 1000 °C, with consequent interface reactions that decrease the efficiency and stability of the cell. To overcome such drawbacks, main research efforts are currently addressed to new materials able to lower the operating temperature (then reducing interfacial ageing processes), the development of stack technology based on planar supported electrode configuration and more active, less poisonous electrocatalysts.

Moreover, the current approach of reducing the operation temperature (up to 700 °C) would allow a wider choice of low cost materials, particularly for the interconnection (metallic) and the sealant, a longer cell life-time due to lower interdiffusion, sintering processes and thermal stress, improved reliability and a reduced overall cost. In this regard, the electrolyte materials of choice, that exhibit high conductivity and sufficient stability, are based on ceria and lanthanum gallate.

Ceria doped with samaria or gadolinia shows a comparable oxygen ion conductivity and a lower conduction activation energy with respect to the traditional yttria-stabilized zirconia (YSZ), with lower reducibility phenomena at low oxygen partial pressure due to the presence of electronic defects. However, CeO_2-based electrolytes are known to display electronic conductivity at relatively high oxygen partial pressures ($pO_2 < 10$ exp-12 atm at 800 °C); thus, in order to meet system efficiency requirements, a reduction in operating temperature to 500 °C was suggested for a more effective use of these materials. A further critical aspect for obtaining good performance resides in the preparation method (raw materials, impurities, sintering conditions, etc.), as well as in the level of homogeneity of rare earth atoms in the sample since conduction is strongly dependent on the concentration of rare earth elements. Also lanthanum gallate doped with Sr, Mg, Co and Fe shows a very high conductivity over a wide range of oxygen partial pressure and is stable in both oxidizing and reducing environments. On the other hand, disadvantages include volatilisation of gallium oxide and formation of secondary phases during processing; the former can be reduced by partial substitution of Ga3+ with other cations, while proper processing conditions can contribute to suppress impurity phases.

However, all the drawbacks connected with the use of these low temperature electrolytes are counterbalanced by the possibility of using stainless steel as structural material for SOFCs, and any materials problem encountered at 1000 °C will be significantly reduced.

In every case, the fabrication procedures to obtain electrolyte layers in thin film form play a decisive role in minimizing the resistance losses. A careful choice of the procedure must also consider aspects such as low-cost manufacture, straightforward scale-up and easy quality control. Sputtering, spray-pyrolysis, electrophoresis, plasma, coating, vapor deposition techniques are the most used and promising both in terms of quality of the layer and cost-effective large scale production.[2–5]

As for the electrodes, nickel- and lanthanum strontium manganite-based materials have been widely investigated and adopted as anode and cathode, respectively, on the basis of prerequisites such as electrocatalytic activity, electrical conductivity, compatibility with the electrolyte and matching in thermal expansion with other cell components. Since in the typical anode-supported cell configuration the cathode is responsible for the major performance loss, especially at low temperature; particular attention has been recently paid to developing more effective microstructures able to extend the triple phase boundary where the oxygen reaction occurs.

The last ambitious goal pursued in SOFC research is the direct oxidation of dry hydrocarbons;[6,7] this configuration would avoid the significant complications derived from the fuel reforming step, resulting in a more simplified plant scheme, with obvious technological and economic advantages. The research challenge to be won is, in this case, to avoid the severe carbon deposition phenomena that are thermodynamically favoured under these conditions. To date, the most active effective anode catalyst is based on the Cu–CeO_x system, since copper poorly catalyses the C–H bond activation and ceria promotes the hydrocarbon oxidation. However, some attention must be paid to the hot fuel supply zones; the steel piping and tubing would require some specific protection in order to avoid any carburisation phenomena.

The reaction mechanism gives a fundamental importance to the catalyst composition, the interaction with the reagent and the morphology of the electrode structure. The optimisation of these parameters is a complex route that, if successful, will permit us to reach energy densities very close to those required for practical applications. Particularly in this case, time-life tests will be very important to assess the achievable performance of the different catalyst formulations under investigation. Not least, a proper choice of some operationing conditions would allow us to drive a kind of "internal reforming" performed by the water generated during the reaction, that would enhance the reliability and durability of the catalyst.

4. Ceramic membranes for oxygen pumping and syngas production

Getting high purity oxygen from air has many potential benefits in the framework of the energy–environment relationship, allowing us to reduce, for example, harmful emissions from diesel engines, coal and hydrocarbon gasification plants, as well as in synthetic fuel production; moreover, an oxygen separation membrane integrated with a fuel cell can lead to relevant advantages in terms of performance.

The oxygen pumping materials and processes can be schematically classified in terms of the driving force mechanism that governs oxygen separation. Accordingly, oxygen ion conductors with low or absent electronic conductivity can be used when a voltage is applied across them to separate and compress oxygen from a low pressure source. Reduction and evolution of oxygen occurs at the anode and cathode compartments, respectively. The current flowing through the device determines the oxygen flux rate, which also depends on the electrical resistance of the device and the applied voltage signal; these latter are in turn determined by the nature of electrode materials, operation temperature and conductivity of the ceramic membrane under the selected conditions.

Alternatively, mixed ionic–electronic conductors can be included into processes which impose an oxygen partial pressure differential across the membrane; this drives oxygen ions from the high partial pressure side to the low one. The electrons in the membrane combine with oxygen in the air creating oxygen ions; no electrodes are required with this configuration. The main technical challenges to be faced are the stability of the materials and seals with the required performance characteristics, which will sensibly affect the cost of the device and its lifetime.[8,9]

Oxygen separation membranes also represent a cost-effective alternative to the production of synthesis gas (H_2+CO) from natural gas, at present generally done by steam reforming, which is an energy- and capital-intensive process.[10] Air flows on one side of the membrane while methane flows on the other side. Because the membrane is permeable to oxygen but not to nitrogen, oxygen diffuses through the membrane; electrons in the membrane combine with oxygen to create negatively charged oxygen ions. The ions migrate through the membrane, from the air side to the natural gas side, where the electrons are stripped from the ions, converting them into oxygen atoms, which combine with methane to form syngas. The electrons migrate back to the air side of the membrane, create fresh oxygen ions, and the process continues.

The high ($>98\%$) efficiency of such a system and the low cost of oxygen results in an overall cost abatement for the natural gas–syngas conversion of 30%.

Amongst the oxygen ion conductors, the fluorite structure oxides, such as cubic stabilised zirconia and gadolinia-doped ceria (also used for SOFCs) have been attracted considerable attention. On the other hand, most of the mixed conductors of technological interest have the ABO3 perovskite structure, belonging to the $LnCoO_3$ class characterized by high oxygen permeability (for example, $La_{1-x}Sr_xCoO_{3-y}$, LSCs). The poor thermochemical and mechanical properties of this material can be enhanced by co-doping with iron on the B-site (LSCFs), but this gives rise to a lower oxygen flux. The most investigated material in recent years is the mixed conductor $SrFeCo_{0.5}O_x$, which displays high oxygen fluxes together with a greater chemical and mechanical stability than LSCs, LSCFs and fluorites. More recent studies concern La_2NiO_4-based ceramics, for which interesting oxygen–ion transport properties have been disclosed.[11]

5. High temperature proton conductor oxides and membranes for hydrogen pumping

High temperature proton conducting oxides based on perovskite structure are currently investigated because of their potential use in several applications, such as separation membranes, solid state gas sensors, membrane reactors and electrolytes for fuel cells.

The interest for this latter purpose mainly arises from the current unavailability of proton conductive materials in the temperature range 200–500 °C, that hinders the development of a new "breed" of fuel cells with no need of precious metal catalysts and much wider fuel flexibility. On the other hand, the lower temperature of operation, with respect to oxygen ions conductors in SOFCs, would potentially allow easier cell construction, enabling cheaper materials to be used, as well as reducing the problems related to thermal stress.

Perovskite-type materials, such as $BaCeO_3$, $SrCeO_3$ and $BaZrO_3$, are known to exhibit proton conduction in hydrogen and wet atmospheres in the temperature range 200–500 °C, whilst in dry, hydrogen free conditions they have p-type (hole) conductivity. However, to exhibit proton conduction, the presence of oxygen vacancies in the perovskite structure is required; these vacancies can be created through doping with an aliovalent metal ion. Once the doped material is heated in a wet atmosphere, the vacancies are readily occupied by 'transient' hydroxyl ions. Unfortunately, the good (10^{-2}–10^{-3} Scm^{-1}) conductivity exhibited by barium cerate-based ceramics is counterbalanced by their thermodynamic instability towards carbon dioxide and water. The replacement of ceria by zirconia enhances the chemical stability of the material but results in a significantly lower conductivity.[12,13]

Another class of perovskite oxides, with a wider range of compositions and non-stoichiometry without doping, is currently being investigated. These have general formula $A_3\ B'_{1+x}\ B''_{2-x}\ O_{9-d}$ (A divalent, B′ and B″ divalent and pentavalent, respectively). When $x=0$ these materials contain few oxygen vacancies and thus are poor proton conductors; if the stoichiometry is shifted, the formation of oxygen vacancies occurs. Promising results have been shown for the non-stoichiometric $Ba_3CaNb_2O_9$, $Ba_2YsnO_{5.5}$ and $Ba_2In_2O_5$; their effectiveness is however strongly limited by the poor chemical stability in CO_2 and H_2 atmospheres.[14]

Hydrogen separation membranes can find a large application for hydrogenation–dehydrogenation processes in the petrochemical industry, for separation of hydrogen from fossil fuels and reformed natural gas, as well as representing a promising technology able to sequester CO_2 emissions. Compared to metal, polymer and microporous membranes, dense inorganic membranes offer new, interesting chances in terms of high temperature operation, mechanical stability and selectivity.

The hydrogen ions permeation ability of a number of perovskites makes these materials promising for such applications, but several technical and economic aspects have to be examined closely before a practical process can be established.

The pure proton conductor $SrCe_{0.95}Yb_{0.05}O_{3-x}$ perovskite, for example, has been demonstrated to operate as a hydrogen pump in the configuration using two metal electrodes across which a potential difference is established, but the cost-effectiveness of such a system has still to be proven.

Alternatively, a mixed conductor (either single-phase or two-phases material) is able to permeate hydrogen through a chemical potential gradient with no need of electrodes and applied current. Two-phases membranes are $BaCe_{0.4}Zr_{0.4}Gd_{0.2}O_{2.9}$ (BCZG), $SrCe_{0.95}Yb_{0.05}O_{2.975}$ (SCY) and $SrZr_{0.9}Y_{0.1}O_{2.95}$ (SZY), that are proton conductors, mixed with $La_{0.8}Sr_{0.2}CrO_3$ (LSC), which is the electron conducting phase. At present, the two-phases type membrane appears to be favored with respect to single mixed conductors because most of these, being p-type conductors, lose their electron conductivity in reducing environment, which is that of interest for hydrogen pumping.[9–15]

6. Hybrid polymer–inorganic electrolytes for PEM fuel cells

A high temperature operation for PEM fuel cells is thought to be a prerequisite to achieve a significant market penetration of this technology in the short to medium term for both automotive and residential/stationary applications. The development of components able to operate in a higher temperature range (120–150 °C) than the current 70–90 °C can represent a viable option to overcome some of the most critical constraints of the technology which, for many aspects, has been proven to be already mature for practical applications. In automotive, the increase in operation temperature will lead to meet the volume requirements, by reducing the dimensions of the radiator, and to improved overall performance by increasing the tolerance threshold to CO in the reformate fuel. In residential/stationary systems, higher overall efficiencies will derive also from the heat more easily recovered in the cogeneration or heat pump equipment. A key role, in this respect, will be played by the on-going development of composite polymer-inorganic electrolyte membranes with the required specifications of high proton conductivity, low fuel cross-over, high chemical stability and good mechanical characteristics.

Several approaches have been attempted in the last decade to allow high temperature operation with satisfactory cell performance: the incorporation of hydrophilic inorganic material into the perfluorinated ionomer membrane in order to increase the binding energy of water, the use of a non aqueous low volatility solvent to replace water as the proton acceptor within the perfluorinated membrane, or the use of solid state proton conductor able to conduct protons in absence of water; this last approach is the most ambitious, and work is at beginning in this field.

On the other hand, the preparation procedure of hybrid membranes is of crucial importance in satisfying the above said prerequisites. Nanosized inorganic components, for example, will allow the necessary intimate contact with the organic counterpart in order to favour the conduction pathway; the functionalization of oxide particles gives rise to ionic interactions with the organic component, resulting in a significant improvement in mechanical properties.[16]

R&D activities in electrolyte membranes for high temperature operation are countless since PEM technology is thought to be on the eve of commercialization; for a comprehensive survey of the materials tested and results the reader can refer to several reviews on the argument (see for example refs 17–19).

7. Concluding remarks

Electroceramics find wide application in advanced energy technologies as key materials and components in systems that will likely allow to sustain our current living standard in the presence of a strong shortage of resources, a similar demand expansion, and severe environmental constraints.

An intense R&D effort is underway, all over the world, in all the fields of materials science with the aim of making such technologies susceptible of ready commercialization, and so finding consistent answers to that sustainable development which is already a prerequisite if economic growth has to be coupled with the preservation of our life and environment.

A prompt introduction in the market of the above described technologies cannot leave out of consideration the synthesis of properly tailored materials in the presence of appropriate processing procedures, subsequently incorporated in adequate engineered systems.

References

1. European Commission, *Green Paper—Towards a European Strategy for the Security of supply*, 2001.
2. Cacciola, G., Antonucci, V. and Freni, S., *J. Power Sources*, 2001, **1**, 4507.
3. Steele, B. C. H., *Solid State Ionics*, 2000, **134**, 3.
4. Yamamoto, O., *Electrochimica Acta*, 2000, **45**, 2423.
5. Will, J., Mitterdorfer, A., Kleinlogel, C., Perednis, D. and Gauckler, L. J., *Solid State Ionics*, 2000, **131**, 79.
6. Perry Murray, E., Tsai, T. and Barnett, S. A., *Nature*, 1999, **400**, 649.
7. Kim, H., Lu, C., Worrell, W. L., Vohs, J. M. and Gorte, R. J., *J. Electrochem. Soc.*, 2002, **149**, A247.
8. Badwal, S. P. S. and Ciacchi, F. T., *Adv. Mater.*, 2001, **13**, 993.
9. Balachandran, U., Ma, B., Mayia, P. S., Mieville, R. L., Dusek, J. T., Picciolo, J. J., Guan, J., Dorris, S. E. and Liu, M., *Solid State Ionics*, 1998, **108**, 363.
10. Dyer, P. N., Richards, R. E., Russek, S. L. and Taylor, D. M., *Solid State Ionics*, 2000, **134**, 21.
11. Kharton, V. V., Viskup, A. P., Naumovich, E. N. and Marques, F. M. B., *Journal of Material Chemistry*, 1999, **9**, 2623.
12. Kreuer, K. D., *Solid State Ionics*, 1997, **97**, 1.
13. Browning, D., Weston, M., Lakeman, J. B., Jones, P., Cherry, M., Irvine, J. T. S. and Corcoran, D. J. D., *J. of New Mater. Electrochem. Systems*, 2002, **5**, 25.
14. Mukundan, R., Brosha, E. L. and Garzon, F. H., In *ECS Proceedings 2002–5*, 142.
15. Norby, T. and Larring, Y., *Solid State Ionics*, 2000, **136**, 139.
16. Antonucci, P. L., Aricò, A. S., Cretì, P., Ramunni, E. and Antonucci, V., *Solid State Ionics*, 1999, **125**, 431.
17. Savadogo, O. and New Mater, J., *Electrochem. Systems*, 1998, **1**, 47.
18. Inzelt, G., Pineri, M., Schultze, J. W. and Vorotyntsen, M. A., *Electrochimica Acta*, 2000, **45**, 2403.
19. Rikukawa, M. and Sanni, K., *Prog. Polym. Sci.*, 2000, **25**, 1463.