INTRODUCTION

If you ask non-specialists about the role of ceramics in energy conversion and storage, you might get the following type of answer: “Really? I don’t know… But ceramics are yet brittle!” For most users, system engineers and operators, and customers in a broad sense, what matters is that devices work properly and meet the specifications and expectations. What is “inside,” that is, which materials have been developed and used for the application, is at this level not relevant. And even if ceramic materials are essential for a given technology, they are in most of the cases not visible because of the housing necessary for safe operation. That’s why the role of ceramics—although offering unique functionalities—is in general largely underestimated. Furthermore, complex ceramic powders (eg, used as cathode active materials in lithium-ion batteries) or oxide thin films (think about electron-conducting layers in photovoltaics) are rarely considered as ceramics. For all the above-mentioned reasons, ceramics are truly “hidden champions” in this field.

Driven by the urgent need to limit the climate change induced by huge greenhouse gases emissions, the shift from fossil-based energy supply to fluctuating renewables is progressing at a global scale. Numerous studies, papers, and books exist on this exciting and very complex topic of the energy transitions. They are indeed multiple scenarios depending on a large number of factors including political decisions and incentives. Energy technologies are particular in the sense that they are part of a crucial infrastructure. Important selection criteria are investment and operation costs, efficiency, robustness toward dynamic operation and tolerance to pollutants, and long-term reliability. This infrastructure should indeed be resilient and operational for at least 20 years, and often much longer—just think about the general trend of lifetime extension of many nuclear power plants. In a nutshell, there is nothing comparable with consumer electronics and planned obsolescence.

ADVANCED CERAMICS FOR ENERGY CONVERSION AND STORAGE

Advanced ceramics are to be found in numerous established and emerging energy technologies. First, ceramic materials...
possess outstanding thermomechanical properties combined with a high chemical stability, which makes them irreplaceable for high-temperature applications. In gas turbines, advanced ceramic matrix composites (CMCs) reinforced with fibers serve as revolutionary, lightweight structural materials for static and even mobile parts. Ceramic layers such as environmental barrier coatings and thermal barrier coatings are essential for the protection of the underlying metallic or ceramic substrates from corrosion and extreme temperatures, respectively. In nuclear power plants, ceramics are found as sintered nuclear fuels, neutron control materials, moderators, and barriers. Ceramics are also envisaged as host materials to immobilize radioactive waste materials for extremely long times. Receivers for concentrated solar power require materials that absorb sunlight, have a low emission, and withstand high temperatures. Ceramics—both as bulk parts and as coatings—show again unique performance for this technology. Ceramic fillers with high heat capacity are also used for thermal energy storage.

Direct conversion of energy (energy harvesting) is also enabled by ceramic materials. For example, waste heat associated with many human activities can be converted into electricity by thermoelectric modules. Oxide ceramics are stable at high temperature and do not contain any toxic or critical element. Piezoelectrics couple mechanical energy with electric energy, offering the possibility to develop micro-power sources for sensors and electronic devices in hazardous and harsh environments. Functional metal oxide ceramic layers act as essential electron transport medium for both photovoltaics and photo-electrocatalytic water splitting.

Ceramic materials can possess high ionic and/or electronic conductivity too that makes them attractive for electrochemical applications. This electric conductivity is achieved through the design of defects by multiple substitution and doping strategies. Not only high-temperature solid oxide fuel and electrolysis cells (SOFC/SOEC), but also ceramic membranes for oxygen or hydrogen separation from gas mixtures rely on such materials. Both oxygen and proton conductors are interesting from this point of view. Finally, electrochemical storage in rechargeable batteries heavily uses ceramics in the form of complex electrode active materials in state-of-the-art lithium-ion cells and solid electrolytes and separators for emerging and future solid-state batteries. Sodium chemistry offers an interesting alternative, complementary option to lithium chemistry and is well represented by numerous ceramic compounds.

3 | OPPORTUNITIES FOR MATERIAL DESIGN

Independently from the properties and applications targeted, there are common principles for the design, synthesis, and further optimization of ceramic materials. These are the general principles of solid-state chemistry for substitution by iso- or aliovalent ionic species, considering tolerable atomic size ratio for structural stability and enabling the creation of point defects and related changes in oxidation state for electrochemically active compounds. However, there is often a trade-off between performance and stability. For example, the higher the flux through an oxygen transport membrane material, the lower its thermochemical stability toward gases and impurities present during operation. Higher stability can be achieved in multicomponent ceramics by increased configurational entropy, leading to complex compositions for temperature-resistant materials, cathode active materials for lithium-ion batteries, catalysts, etc. And if one phase cannot fulfill all requirements, the development of dual- or triple-phase composite materials can be a paying strategy, as shown in Figure 1.

Due to the infinite number of compositional modifications, unchartered regions of complex phase diagrams cannot be comprehensively investigated from an experimental point of view. In addition, there is a difference between the expected properties of a single crystal or phase and a real polycrystalline ceramic. The effect of pores, complex grain, and phase boundaries and related space charge layers, and eventually dislocations cannot be neglected and even dominates very often the behavior of the ceramic materials. That’s why the use of modeling approaches based on different theoretical frameworks and scales has been reinforced. Ab initio, atomistic ansatz is used for the prediction of crystal properties, molecular dynamics for simulations of charge transport, thermodynamics for phase stability, phase field, or discrete element modeling for the prediction of microstructure evolution. As an example, prediction of charge transfer between

FIGURE 1  Back-scattered electron SEM image of a composite oxygen transport membrane material composed of Ce0.8Gd0.2O2 fluoride (white phase), FeCo2O4 spinel (black phase), and (GdCe)(FeCo)O3 perovskite (gray phase) formed in situ during sintering. Credits: L. Fischer, D. Sebold
ceramic electrolyte and cathode active material is shown in Figure 2. Complex interactions at the atomic level have to be considered. These simulation tools can be nowadays complemented by artificial intelligence and data informatics algorithms in order to take advantage of the large amount of data already published, steadily collected, and evaluated. This approach offers new ways to guide the identification of novel materials that should then synthesized and verified experimentally. Nevertheless, serendipity will certainly further play a role in the discovery of new ceramics and phenomena.

4 | ON THE IMPORTANCE OF MATERIAL INTEGRATION AND PROCESSING

After the synthesis of ceramic powders (usually scalable, a clear advantage for oxide solid electrolytes for solid-state batteries, for instance), numerous processing routes have been developed and are used in the industry for ceramic materials. We took recently the example of yttria-stabilized zirconia (YSZ) to show how both layer thickness from a few atomic layers to thick millimetric coatings and microstructure (from highly porous to fully dense) can be tailored by appropriate processing routes. However, a considerable amount of know-how, not necessarily written in textbooks nor detailed in the scientific literature, is most of the time required for accurate control and reproducibility of the processes and resulting material properties. A practice-oriented, digital handbook or wiki of ceramic processing, summarizing decades of experience, would be very valuable to the scientific community and is to our knowledge still missing.

Integration of ceramic materials into devices is the key to successful transfer in the industry. A material with unprecedented properties is unfortunately useless if not compatible with others when manufacturing a component. In some cases, an intermediate protective layer can offer satisfying functionality, at the expense of simplicity and low total cost. Taking the example of SOFCs, a gadolinium-doped ceria thin film needs to be added between lanthanum-strontium-cobalt-iron-perovskite (LSCF) cathode and YSZ electrolyte to block the inter-diffusion and formation of detrimental phases during sintering.

Huge amounts of energy are required for the consolidation and densification of ceramics at high temperature. These lengthy steps do not vanish with the emergence of additive manufacturing, as most of the time it actually means only shaping of a green ceramic part, likewise requiring an appropriate high-temperature consolidation step. Alternative sintering routes have been therefore proposed in order to decrease time and temperature, assisted by electric fields and currents, mechanical pressure, transient sintering aids, and ultrafast heating. As shown in Figure 3 for lithium-aluminum-titanium-phosphate (LATP) electrolyte, it is possible to densify ceramics at much reduced temperatures compared with free sintering. They might, for instance, bring solutions to the current challenge of co-sintering mixed cathode for solid-state batteries. Still, stringent efforts are required to transfer the accumulated laboratory-scale experience to industrial mass production, but by choosing interesting business cases, new sintering technologies can make their way toward commercialization. Looking back at the development of field-assisted sintering technology/spark plasma sintering over the last years, both diversified product range and automatization have enabled to make use of such innovation.

Alternatively, advanced coating techniques such as plasma-spray physical vapor deposition (PS-PVD) allow for unique microstructures and material combination by evaporating ceramic particles in a hot plasma plume above

![Figure 2](image2.png)

**FIGURE 2** Atomic structure of a probable Li$_2$La$_3$Zr$_2$O$_{12}$/LiCoO$_2$ interface in an all-solid-state battery. (100) and (10-14) are among the most favorable surfaces of Li$_2$La$_3$Zr$_2$O$_{12}$ and LiCoO$_2$, respectively. Credits: LY Kuo, P. Kaghazchi

![Figure 3](image3.png)

**FIGURE 3** Fracture surface of cold sintered LATP (max. temperature: 500°C, pressure: 300 MPa, 1 min dwell time, 1 M LiOH aqueous solution as sintering aid, FAST/SPS as heating unit). Credits: K. Nur, D. Sebold
10,000 K. For instance, a dense hydrogen transport ceramic membrane could be deposited on a porous metallic support with satisfying performance.\textsuperscript{18}

5 | ON THE IMPORTANCE OF TESTING UNDER REALISTIC CONDITIONS

After having solved the challenge of material integration, appropriate testing should be carried out, mimicking possible real operation conditions, operando characterization, and test of working devices being of course the ultimate goal. Due to the long lifetime of energy infrastructure, this demands long-term experiments in realistic environments (ie, relevant temperature range and mechanical loading, “dirty” atmospheres with the presence of water vapor, CO\textsubscript{2}, impurities, etc).

As first example, foreign particles such as calcium-magnesium-aluminum-silicates (CMAS) are particularly detrimental to high-temperature barriers as shown in Figure 4, because they melt and react with the ceramic coating.\textsuperscript{19} Top layers are thus of limited applicability if they only offer high resistance to water corrosion but poor stability in the presence of additional contaminants.

Second, ceramic materials for batteries can be sensitive to air even at room temperature: Some cathode powders need to be handled in dry rooms with extremely reduced water vapor levels. Lithium-lanthanum-zirconate garnet, a promising solid electrolyte, suffers from lithium-proton exchange and formation of carbonates at its surface, leading to a rapid degradation of properties. Fortunately, adequate thermal post-treatments can be carried out so that shaping from water-based slurries can still be done in air, eliminating the large costs for a dry environment as required for liquid organic electrolytes.\textsuperscript{20}

Therefore, changes in mechanical, chemical, electrical, and electrochemical properties should be thoroughly analyzed and related to the phenomena occurring at the micro-structural level. Diffusion, migration, depletion, formation of new phases, coarsening, etc are common events observed in ceramic-based energy technologies after operation, cycling, and/or exposure to typical loadings. Owing to the targeted long lifetime and reliability, it is important to emphasize that not only the first few cycles or the few hours are important: The performance should be monitored over a larger number of cycles or longer period of time, with respect to the requirements for operation.\textsuperscript{3}

As those tests are costly and mobilize infrastructure and manpower, accelerated testing is desirable. However, the difficulty lies in the fact that kinetics only should be modified, and not the nature of the mechanisms involved. Modifying one or several of the testing parameters (temperature, mechanical load, fuel concentration, current density, applied voltage, etc) may indeed trigger other phenomena, which are inexist-ent under normal operating conditions! Early detection, with more precise characterization tools coupled with simulations, could accelerate the pace of research and development. But again, the whole technical system has to be considered and not only one single material or layer. Exemplarily, steels used as interconnectors and frames for the SOFC technology optimized for temperatures above 700°C failed when employed at a lower temperature.\textsuperscript{21}

6 | CONCLUSION

Due to their unique properties, ceramic materials are critical for many energy conversion and storage technologies. In the high-temperature range typically above 1000°C (as found in gas turbines and concentrated solar power), there is hardly any competition with other types of materials. Under the harshest conditions, even new structural ceramic materials such as CMCs\textsuperscript{3} and MAX phases\textsuperscript{22} need protective layers, of course out of stable oxide ceramics. For other applications, especially fuel cells and electrolysis, separation membranes, and batteries, other material classes cannot be neglected. Some interesting options might rely on the combination of organic and inorganic materials, joining respective strengths and eliminating weaknesses in hybrid concepts. To rationally select a technology, the capital and operation costs and life cycle assessment of the whole technical system have to be considered. As mentioned in the introduction, our future energy supply based on renewables will rely on numerous, complementary technologies, where ceramics play for sure—either in mass or niche markets—an important role. To conclude, new aspects related to concepts of circular economy should be considered: repair of components, reuse, and recycling of materials instead of throwing
everything away—this is also relevant for ceramic-based energy technologies!

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