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Proton- Conducting Ceramics

From Fundamentals
to Applied Research



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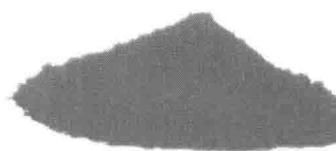
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Foreword

Three Decades of Ceramic Proton Conductors: The Road to Commercialization

Two pivotal events took place in 1981 forever shaping the future of the field of protonic conduction in solids. In that year, the first conference on Solid State Protonic Conductors was organized by Philippe Colomban, and convened in Paris as a joint Danish–French working group. By this time there was sufficient interest in solid proton conductors to warrant such a meeting. In that same year, Hiroyasu Iwahara and colleagues¹ published a paper in the journal *Solid State Ionics* entitled “Proton Conduction in Sintered Oxides and its Application to Steam Electrolysis for Hydrogen Production”. The significance of the discovery of high-temperature ceramic proton conductors by Iwahara cannot be overstated, but the paper went largely unnoticed for years. The Danish–French workshop, now referred to as SSPC-I,² was focused broadly on proton conduction in solids, and the connection to proton transport in perovskite ceramics at elevated temperature was not fully appreciated at that time. The proceedings of SSPC-I, II, and III were published by the Odense University Press, and beginning with SSPC-4 (1988), the proceedings were published in the journal *Solid State Ionics*.³ This meeting in Exeter, Great Britain, was the first SSPC Conference attended by Dr. Iwahara. Even as late as 1989, Robert Slade,

¹Iwahara, H., Eska, T., Uchida, H., and Maeda, N. (1981). Proton conduction in sintered oxides and its application to steam electrolysis for hydrogen production, *Solid State Ionics*, **3/4**, pp. 359–433.

²Thomas J.O., SSPC-12 Chairman (2005). Preface to the Special Proceedings of the 12th International Conference on Solid State Proton Conductors, *Solid State Ionics*, **176**, p. 2837.

³Slade R.T., SSPC-4 Chairman (1989), Preface to the Special Proceedings of the 4th International Conference on Solid State Proton Conductors, *Solid State Ionics* **35**, pp. 1–2.

chairman of SSPC-4, mentioned “the relatively new field” of protonic electrolytes and commented in the proceedings preface, “The development of create protonic conductors for high temperatures was both a major step forward and also contrary to the accepted wisdom that ceramic processing precludes protonic conductivity”. This statement expresses the skepticism that existed for nearly 10 years after Iwahara’s discovery.

The story of Iwahara’s discovery of ceramic proton conductors actually dates back considerably further. The first suggestion of proton conduction in lanthanum aluminate ceramics was by the Frenchman Francis Forrat and coworkers in 1964.⁴ Shortly thereafter, the possibility of high-temperature hydration by filling oxygen ion vacancies in ceramic oxides with hydroxyl ions was formally proposed by Stotz and Wagner in 1966.⁵ Forrat mistakenly attributed proton transport to cation vacancies in what was thought to be $\text{AlLa}_{(1-x)}\text{H}_x\text{O}_3$. Iwahara later showed, however, that the correct formulation for doped lanthanum aluminate is $\text{La}_{(1-x)}\text{M}_x\text{AlO}_{3-\delta}$ and that the conductivity observed by Forrat was probably due to oxygen ions on the anion sublattice. Nonetheless, the possibility of proton conduction in ceramics at elevated temperatures was out in the open. Armed with practical experimental techniques in high-temperature solid-state electrochemistry, Iwahara and Takahashi carried out the first systematic investigation of ionic conduction in perovskite ceramics, published in 1971.⁶ Throughout the seventies, they improved their experimental techniques and recognized the unusual emf behavior in certain perovskites that could only be explained by proton transport. Iwahara and Takahashi published their original paper on proton conductivity of lanthanum–yttrium oxide and strontium zirconate in 1980 in a rather obscure French journal,⁷ which had almost no impact on the field for many years.

⁴Forrat F., Dauge G., Trevoux P., Danner G., and Christen M. (1964). Electrolyte solide à base de AlLaO_3 . Application aux piles à combustible, *Comptes Rendus de l'Académie des Sciences*, **259**, p. 2813–2816.

⁵Stotz V.S. and Wagner C. (1966). Die Löslichkeit von Wasserdampf und Wasserstoff in festen Oxiden, *Berichte der Bunsengesellschaft für physikalische Chemie*, **70**, pp. 781–788.

⁶Takahashi T. and Iwahara H. (1971). Ionic conduction in perovskite-type oxide solid solutions and its application to the solid electrolyte fuel cell, *Energy Conversion*, **11**, pp. 105–111.

⁷Takahashi T. and Iwahara H. (1980). Solid state ionics: Proton conduction in perovskite type oxide solid solutions, *Revue de Chimie Minérale*, **17**, p. 243.

In the introduction it is claimed that, "The present authors have found that the solid solutions based on lanthanum–yttrium trioxide (LaYO_3) and strontium–zirconium trioxide (SrZrO_3) could show a proton conduction in hydrogen gas. The proton conduction in these solid solutions has been confirmed by an electrochemical method." It is this paper that properly marks the invention of ceramic proton conductors, and it is surprising today that this historic discovery went virtually unknown for years. John Goodenough did not mention Iwahara's work in his review of the status of ceramic proton conductors presented at SSPC-II in 1982.⁸

Notwithstanding the slow start, Iwahara envisioned hydrogen–air fuel cells, steam electrolysis cells, hydrogen separation membranes and hydrogen sensors from the very beginning. The steam concentration cell was proposed as a way to "recover energy from exhaust gas . . . in industrial plants" in 1982.⁹ An important new branch of protonic ceramic applications in membranes for hydrogenation and dehydrogenation of hydrocarbon gases was first demonstrated by Iwahara in 1988.¹⁰ This paved the way for the important commercial applications as membrane reactors demonstrated by Hamakawa's group¹¹ and the advent of methane dehydroaromatization as a method for converting natural gas to liquids by a non-oxidative route. In a review paper in 1992,¹² Iwahara identified 12 diverse applications for ceramic proton conductors, which he had demonstrated in his lab that provided compelling evidence for the utility of the technology. These were broadly classified as (1) sensors, (2) fuel cells, (3) hydrogen separation, (4) electrolyzers, and (5) membrane reactors. In a presentation in Schwäbisch, Germany, at SSPC-7 in 1995, Iwahara described 15

⁸Goodenough J.B. (1982), Solid state ionic conductors, Proceedings of SSPC-II, Hindsgavl Castle, Denmark, Odense University Press, pp. 123–142.

⁹Uchida H., Maeda N. and Iwahara H. (1982). Steam concentration cell using a high-temperature type proton conductive solid electrolyte, *Journal of Applied Electrochemistry*, **12**, pp. 645–651.

¹⁰Iwahara H. (1988). High-temperature proton-conducting oxides and their applications to solid electrolyte fuel cells and steam electrolyzer for hydrogen production, *Solid State Ionics*, **28–30**, pp. 573–578.

¹¹Hamakawa S., Hibino T., and Iwahara, H. (1993). Electrochemical methane coupling using protonic ceramics, *Journal of the American Ceramic Society*, **140**(2), pp. 459–462.

¹²Iwahara H. (1992). High-temperature protonic conductors and their applications, *Solid State Ionics*, **178**(7–10), pp. 575–586.

commercial applications for ceramic proton conductors, which he claimed were “positively verified to work”. This paper entitled “Technological Challenges in the Application of Proton-Conducting Ceramics”,¹³ provides a virtual road map for commercialization of the technology. The only significant application for ceramic proton conductors that Iwahara did not mention—solid state ammonia synthesis and the corresponding ammonia fuel cell—were demonstrated for the first time by Marnellos and Stoukides in 1998.¹⁴ These electrochemical applications and a host of non-galvanic devices using mixed ionic/electronic protonic conductors, cermets, and cercers were widely considered to be commercially viable by 2000. How is it possible, then, that as of 2014 there is still no successful commercial product except a small sensor initiative?

By contrast, the transistor was discovered in 1947, and already by 1956 Sony had transistor radios on the market. The technical feasibility of ceramic proton conductors for many applications had been demonstrated by 2000, but unlike early germanium transistors, commercial viability was lacking. The problem was one of finding suitable materials. By happy coincidence, germanium crystals of sufficient purity were already available in 1947, so that transistors could be fabricated that worked well enough for early commercial applications. This gave impetus to semiconductor development through relatively short product development cycles that led to silicon and the proliferation of devices enabled by it. No such development was possible for ceramic proton conductors, because there was no material that worked well enough for commercialization. The first successful commercial application for ceramic proton conductors was for a hydrogen sensor based on In-doped calcium zirconate at TYK Corp., and is sold today under the tradename “Notorp”. The first commercialization initiative for protonic ceramic fuel cells was Protonetics International, Inc., in 2000. The leading candidate material at the time was yttrium-doped barium cerate, BCY, but when it became apparent that BCY was chemically unstable in carbon dioxide and steam under the operating conditions, the company was

¹³Iwahara H. (1995), Technological challenges in the application of proton-conducting ceramics, *Solid State Ionics*, **77**, pp. 289–298.

¹⁴Marnellos G. and Stoukides M. (1998), Ammonia synthesis at atmospheric pressure, *Science*, **282**, pp. 95–98.

folded shortly thereafter, and it was “back to the drawing board” to find a more suitable material.

Once it became widely recognized that pure perovskite cerates would probably never be useful for widespread commercial application, attention was focused on developing more stable ceramic proton conductors. Yttrium-doped barium zirconate (BZY) was a leading contender, championed most notably by Klaus Dieter Kreuer during the 1990s,¹⁵ but the material proved almost impossible to sinter using solid state reaction to prepare the precursor powders followed by tradition ceramic sintering. This necessitated the use of more exotic sintering methods not well suited for commercial production. Furthermore, the ceramic materials tended to have small grains with high grain boundary resistance to proton transport. The critical breakthrough came in 2004 by the discovery of solid state reactive sintering by Babilo and Haile.¹⁶ They demonstrated that dense, large-grained BZY could be fabricated in a single processing step from precursor powders, BaCO_3 , ZrO_2 , and Y_2O_3 , with the addition of a small amount of sintering additive such as ZnO . The process is generally now called solid-state reactive sintering. The impact of this discovery on commercial development of ceramic proton conductors cannot be overstated. It may be compared to the discovery of zone refining in semiconductor technology, which made it possible to grow silicon crystals with sufficient intrinsic purity to allow p- and n-type doping for manufacturing practical transistors. With solid state reactive sintering (SSRS), it became possible to fabricate practical ceramic proton conductors over the full range of BCY to BZY. $\text{BaCe}_x\text{Zr}_{(0.9-x)}\text{Y}_{0.1}\text{O}_{3-\delta}$, BCZY, is an acceptor-doped cubic ABO_3 perovskite proton-conducting ceramic constituting a complete solid solution between the end members, barium cerate, and barium zirconate, for $0 \leq x \leq 0.9$. The series has been recognized for many years as, perhaps, the ideal ceramic proton conductor, but compositions containing more than a few mol% Zr proved almost impossible to sinter into a dense polycrystalline ceramic until the discovery of solid-state reactive sintering. With SSRS, making dense

¹⁵Kreuer, K.D. (1999). Aspects of the formation and mobility of protonic charge carriers and the stability of perovskite-type oxides, *Solid State Ionics*, **125**, pp. 285–302.

¹⁶Babilo, P. and Haile, S.M. (2005). Enhanced sintering of yttrium-doped barium zirconate by addition of ZnO , *Journal of the American Ceramic Society*, **88**(9), pp. 2362–2368.

and gas-tight BCZY membranes at a commercial scale became possible for the first time.

The question of how long it should take between demonstrating technical feasibility and commercial viability is an important question for research scientists and engineers, because ultimately commercial viability determines the availability of the required investment capital. Is 30 years too long? The silicon semiconductor story is perhaps misleading and has given unrealistic expectations about how long commercialization of new technology should actually take. The more appropriate analogy in semiconductor development may be found in the III–V semiconductors. It was known almost from the invention of the transistor that direct bandgap compound semiconductors like GaAs offered superior properties, such as faster operation, but making crystals of the materials with sufficient purity turned out to be a daunting challenge. The first commercial application did not become widely available until Sony and Phillips brought the semiconductor laser to market in the form of the compact disc player in 1978—31 years after the invention of the transistor. Even more compelling is the story of wide bandgap light-emitting diodes. The first red LEDs based on GaAs were produced by Monsanto in 1961, but another 30 years were required before the first blue LEDs based on GaN were produced—not because scientists did not know what to look for—but because many materials science challenges had to be overcome. Another 20 years were required before blue LEDs would find their way into commercial applications for high-efficiency light sources by companies like Phillips and Cree. It is easy to think that commercialization should come quickly for innovations as disruptive as ceramic proton conductors, but the pacing element with these, as with semiconductor devices, generally rests with materials scientists. The pace of commercialization cannot advance any faster than the understanding of how to prepare the necessary materials with the pre-requisite properties for the intended applications.

The chapters in this new book constitute the most comprehensive and most up-to-date compilation of the science and technology of ceramic proton conductors. The following chapters attest to the enormous progress that has been made over the past three decades by many of the leading scientists working in the field today. Although there is still much to be learned, devices are now being fabricated

using ceramic proton conductors that exhibit the necessary properties for various commercial applications envisioned by Dr. Iwahara 30 years ago, and I am confident that this technology is now poised to revolutionize the field of energy sustainability in much the same way that the transistor has revolutionized the information age.

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Preface

The worldwide energy demand and the associated increasing environmental concerns has driven research more and more to find alternatives for clean energy source. In such context, the hydrogen economy has continuously grown since 1970s—date of the first worldwide oil crisis.

Now, the trend is ready to promote the use of hydrogen as an energy carrier in many strategic fields (transportation, distributed energy conversion, gas separation . . .). In particular, the research of high- performing and reliable ionic-conducting materials likely to valorize hydrogen source is fundamental. In such matter, two kinds of ionic conducting material-based technologies coexist in the research and development:

- The polymer-based technology used at low-temperature domain below 300°C.
- The ceramic-based technology used at high-temperature domain above 400°C.

Among the possible cation and anion conduction studied, the proton is found in many different solid materials, from organic polymers at room temperature to inorganic oxides (such as ceramics and solid acids) at higher temperatures beyond 300°C. For more than 40 years, it has played a very important role in many processes implying diverse phenomena in biology, chemistry, or physics. Especially, several studies have been carried out in the field of proton-conducting membranes as electrolyte in the hydrogen chain related to energy conversion and storage applications.

Thus, while proton-exchange polymer-based membranes (commonly named PEM) are commercially used in the low-temperature domain, proton-conducting ceramic-based materials (labeled PCC) remain at an early stage of development at higher temperatures. Notably, PCC technology has come up against the merging of commercial oxygen ions O_2 -conducting solid oxide cell (noted SOC) beyond 700°C.

However, such high operation temperature implies the use of costly ceramic materials into complex fabrication and the need for an important energy input to achieve relevant cell performance. Besides, it imposes to ceramic-based technology high thermal stresses caused by thermal expansion mismatch of materials and therefore limited operation profiles (low start-up kinetics, low thermal cycling). As we can guess, the performance of such energy systems highly depends on the properties of their core components, thus requiring the synthesis and the development of high performing and reliable ones, in particular, the ionic conducting electrolyte membrane which constitutes the heart of the electrochemical device.

Thereby, intensive researches are yet being deployed for appointing advanced generation of ceramic-based materials able to operate at intermediate temperature between 400 and 700°C while keeping reasonable performance and reliability. This lower temperature of operation will allow easier cell construction, enabling cheaper materials to be used, and will reduce the problem of thermal stress.

In such quest, the theoretical intrinsic specificities of the proton element (smallest size, high diffusion kinetics, etc.) brings better electrical pathway in electrochemical devices versus the oxygen ions. In particular, below 700°C, the proton-charge carriers become advantageous for coupling higher kinetic and lower activation energy needed in a ceramic matrix.

The last two decades revealed the merging of new families of ceramic oxides on the basis of proton transport, which have the main advantage of running at intermediate temperatures with better electrical and mechanical properties than common SOC. They are considered as promising electrolyte candidates for high-efficiency electrochemical devices related to energy applications such as fuel cell, water electrolysis system, hydrogen and humidity sensors, catalytic membrane reactors, etc.

Many reviews and scientific articles have covered all main aspects of PCC research starting from proton transport mechanism principles to their synthesis and cell manufacturing techniques. However, the refractory nature, the extreme process conditions, the chemical stability toward carbon dioxide and water or the complex transport phenomena mechanisms of the currently prevailing

proton-conducting ceramics remain as some important challenges to propose their implementation in such devices.

And now, after 20 years of research and development, where are we? What is the real value of PCC technology? Is it competitive with conventional solid oxide technology? Can we consider any strategic R&D pathways to deal with a profitable PCC market?

This book tends to humbly reply to such questions by joining in the same approach some educational aspects of PCC technology for the novices and some critical point of views of scientist experts in the domain by promoting strategic routes for contributing to the PCC merging market.

In this sense, the current book is based on four sections, dealing with topics from raw materials to system applications.

Chapter 1 consists of three sections that deal with theories and principles from the proton hydration process to the transport properties through the ceramic matrix. It proposes notably some main characterization tools likely to illustrate the proton presence.

Chapter 2 aims to give us an updated background of the most promising families of proton-conducting ceramic oxides studied by assessing their structural characteristics and their main intrinsic chemical and electrical properties. For that, five types of material oxides are considered:

- the perovskite structure-based oxides
- the acceptor-doped metal oxides
- the fluorite structure-based oxides
- the pyrochlore structure-based oxides
- another more “exotic” type oxides

Chapter 3 lists the main conventional and promising techniques for the elaboration of compound materials of the cell with respect to technical and structural specifications required for each layer of cell. A special attention is brought to the industrialization level of synthesis and manufacturing methods.

The last chapter, Chapter 4, of the book includes four sections, each of which deals with the use of proton-conducting ceramics in the most promising applications advised by the expertise of co-authors:

- the proton-conducting material as an electromotive force

- the proton-conducting material as an electrochemical hydrogen transport
- the proton-conducting cell in solid-state ammonia synthesis

It should be noted that at the end of each section, a short summary is proposed by including the main key points and recommendations of co-authors.

Finally, I would like to acknowledge the support of all co-authors who have expended huge “extra” time beyond their professional time schedule to write and affine the description of this book. Its success would also be their success . . .

Mathieu Marrony
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