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Introduction and Overview: Protons, the Nonconformist Ions

Maria Luisa Di Vona and Philippe Knauth

“The Nonconformist Ion” is the title of a review article on proton-conducting solids by Ernsberger in 1983 [1]. Indeed, many proton properties are peculiar. First of all, the very particular electronic structure is unique: its only valence electron lost, the proton is exceptionally small and light and polarizes its surroundings very strongly. In condensed matter, this will lead to strong interactions with the immediate environment and very strong solvation in solution.

Second, two very particular proton migration mechanisms are well established. In “vehicular” motion, a protonated solvent molecule is used as a vehicle. This mechanism is typically characterized by higher activation energy and lower proton mobility. In structural motion, the so-called Grotthuss mechanism involves site-to-site hopping between proton donor and proton acceptor sites with local reconstruction of the environment around the moving proton. This mechanism is related to lower values of activation energy and higher proton mobility.

Proton conduction can be found in many very different solid materials, from soft organic polymers at room temperature to hard inorganic oxides at high temperature. The importance of atmospheric humidity for the existence and stability of proton conduction is another common point, which goes with experimental difficulties for measuring proton conductivity in solids.

Proton-conducting solids are the core of many technological innovations, including hydrogen and humidity sensors, hydrogen permeation membranes, membranes for water electrolyzers, and most importantly high-efficiency electrochemical energy conversion in fuel cells working at low temperature (polymer electrolyte membrane or proton exchange

membrane fuel cells, PEMFC) or intermediate temperature (proton-conducting ceramic fuel cells, PCFC).

1.1 Brief History of the Field

Proton mobility is a special case in the field of ion transport. In early textbooks on the electrochemistry of solids, proton-conducting solids are not even mentioned [2], except ice [3].

Historically, the existence of protons in aqueous solutions had already been conjectured by de Grotthuss in 1806 [4]. The study of proton-conducting solids started at the end of the nineteenth century, when it was noticed that ice conducts electricity, with the investigation of the electrical conductivity of ice single crystals [5]. A first mention of “vagabond” ions in an inorganic compound, hydrogen uranyl phosphate (HUP), was due to Beintema in 1938 [6]. However, it was not until the 1950s that the study of solid proton conductors started in earnest: Bjerrum’s fundamental study on ice conductivity led the way in 1952 [7], and Eigen and coworkers discussed the proton conductivity of ice crystals in 1964 [8]. Nevertheless, these investigations were fundamental studies and the materials could still be considered only laboratory curiosities.

The first proton-conducting material applied in practice was a perfluorinated sulfonated polymer, Nafion, adapted by DuPont in the 1960s as a proton-conducting membrane for PEMFC, used in the Gemini and Apollo space programs. This gave important momentum to the domain of solid proton conductors. Several inorganic solid proton conductors were then reported in the 1970s and 1980s. The rediscovery of HUP was followed by the discovery by Russian groups of several acid sulfates showing structural phase transitions, such as CsHSO_4 [9] and zirconium hydrogenphosphate (ZrP), by Alberti and coworkers [10]. Furthermore, oxide gels containing water show nearly always some proton conductivity [11]. However, with the exception of ZrP, the proton conductivity of these materials is limited to about 200 °C.

An important discovery was, therefore, the report by Iwahara and coworkers in the 1980s of “high-temperature” proton conduction in perovskite-type oxides in humidity- or hydrogen-containing atmosphere [12], where the maximum of proton conductivity is typically observed at temperatures above 400 °C.

Nowadays the main fields of development are proton-conducting polymer membranes for low-temperature applications and proton-conducting oxide ceramics for intermediate- and high-temperature devices. Given the current interest for the possible future hydrogen economy, the fuel cell field is mentioned in most articles of this book.

1.2 Structure of This Book

The most recent textbook on all aspects of solid state proton conductors was published in 1992 [13]. Excellent review papers have been published afterward, for example by Norby in 1999; [14] Alberti and Casciola in 2001 [15]; and Kreuer, Paddison, Spohr, and Schuster

in 2004 [16], but an updated textbook summarizing the current knowledge on solid state proton conductors seemed worthwhile.

In the following chapters, some of the leading experts in the field have written authoritative review chapters on the characterization techniques, modeling, and properties of solid state proton conductors.

The chapter “Morphology and Structure of Solid Acids” shows an overview of structural analysis of some important solid acids by scanning electron microscopy. This beautifully illustrated chapter is an aesthetic pleasure, and the micrographs are complemented by polyhedral representations and a short introduction on the technique.

The chapter “Diffusion in Solid Proton Conductors: Theoretical Aspects and Nuclear Magnetic Resonance Analysis” starts with an overview on fundamentals of diffusion. Then, principles of nuclear magnetic resonance (NMR) spectroscopy are introduced. Nuclear magnetic resonance is a very powerful technique for investigation of structure and diffusion in solid proton conductors; NMR imaging is a newer development, and is also addressed on a basic level in this chapter.

The chapter “Structure and Diffusivity in Proton-Conducting Membranes Studied by Quasi-elastic Neutron Scattering” introduces the basics of neutron scattering, which is obviously of particular importance for the field. Analysis of diffusional processes in inorganic as well as organic solid proton conductors is presented and discussed.

The chapter “Broadband Dielectric Spectroscopy: A Powerful Tool for the Determination of Charge Transfer Mechanisms in Ion Conductors” is devoted to the electrical properties of ion-conducting solids, especially macromolecular systems. This chapter describes fundamentals and examples of dielectric measurements in a broad frequency domain, which can be used for a wide range of materials from insulators to “super-protonic” conductors.

The chapter “Mechanical and Dynamic Mechanical Analysis of Proton-Conducting Polymers” introduces first some basic principles of the mechanics of materials: elastic and plastic deformation, creep and relaxation, and dynamic mechanical analysis. Then, the mechanical properties of proton-conducting polymers and their durability are discussed.

The chapter “Ab Initio Modeling of Transport and Structure of Solid Proton Conductors” presents a rapid introduction on the theoretical methods of choice. Significant examples of solid proton conductors are discussed, including proton-conducting polymers; solid acids, such as CsHSO_4 ; and proton-conducting perovskite oxides.

Two chapters are devoted to polymeric proton conductors. The chapter “Perfluorinated Sulfonic Acids as Proton Conductor Membranes” introduces the field and presents recent progress for the improvement of the oldest but still leading ionomer, Nafion. This chapter reviews a physicochemical approach and strategies for future enhancement of the durability of Nafion membranes.

The chapter “Proton Conductivity of Aromatic Polymers” discusses a main family of alternative ionomers based on fully aromatic polymers. Their synthesis and electrical properties and further possibilities for improvement, such as hybrid organic–inorganic ionomers and cross-linked systems, are discussed.

The last chapter reviews “Inorganic Solid Proton Conductors.” The chapter recalls fundamentals of ionic conduction in inorganic solids and presents the main classes of proton-conducting materials, including layered and porous solids, “quasi-liquid” structures, and defect solids, especially perovskite oxides.

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