

Protonic Ceramic Fuel Cells as novel electrochemical devices

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ABSTRACT

Proton ceramic conductors are novel materials which are interesting from the application point of view. For example, Protonic Ceramic Fuel Cells (PCFCs) is a type of a solid oxide fuel cell, which uses proton ceramic conductors as an electrolyte. Scientists are looking for the most efficient materials for these devices. In recent years main focus has been put on the search for new proton and mixed proton-electron conductors which could be applied as electrolytes or electrodes.

Keywords:

Electrical energy demand, fuel cell, protonic conductors

1. INTRODUCTION

Global demand for electrical energy is still rapidly increasing [1]. Due to technology advancement human population use more and more electrical devices. Electrical energy has been used since 16th/17th century. The scientific revolution took off at the end of the 16th century, and it was mainly concerned with mechanics and medicine [2]. Groundbreaking discoveries performed by Gilbert, Coulomb, Volta and many others were a milestone in understanding the laws of electricity. Their achievements in electric engineering were inspiring for the future inventors. For decades people has been trying to improve present technologies. The main reason of this is the tendency to improve the quality of our lives. Current energy production is based mostly on fossil fuels, which deposits are predicted to be exhausted in several decades. Therefore, nowadays scientists are looking for new sources of energy. Numerous scientific groups are focusing on renewable energies. Moreover, people also need sources of energy which could power up for example cars, buses or trains [3]. This demand can be fulfilled by the fuel cell

technology. It should be stressed that currently, several companies produce buses or cars powered by fuel cells [4], but they are usually not solid oxide fuel cells.

2. FUEL CELLS – PRINCIPLES OF OPERATION

A fuel cell is an electrochemical device which produces electrical energy through the chemical reactions. First fuel cells were invented in the 19th century [5]. The main components of a fuel cell are two electrodes (anode and cathode) and an electrolyte separating layer.

In order to produce energy out of a fuel cell, the fuel has to be continuously supplied to the device. The most efficient fuel is hydrogen, which must be delivered to the anode. On the other electrode, the cathode, oxidizing agent, for example, oxygen or air, must be delivered. These principles of fuel cell operation are shown schematically in **Fig. 1**.

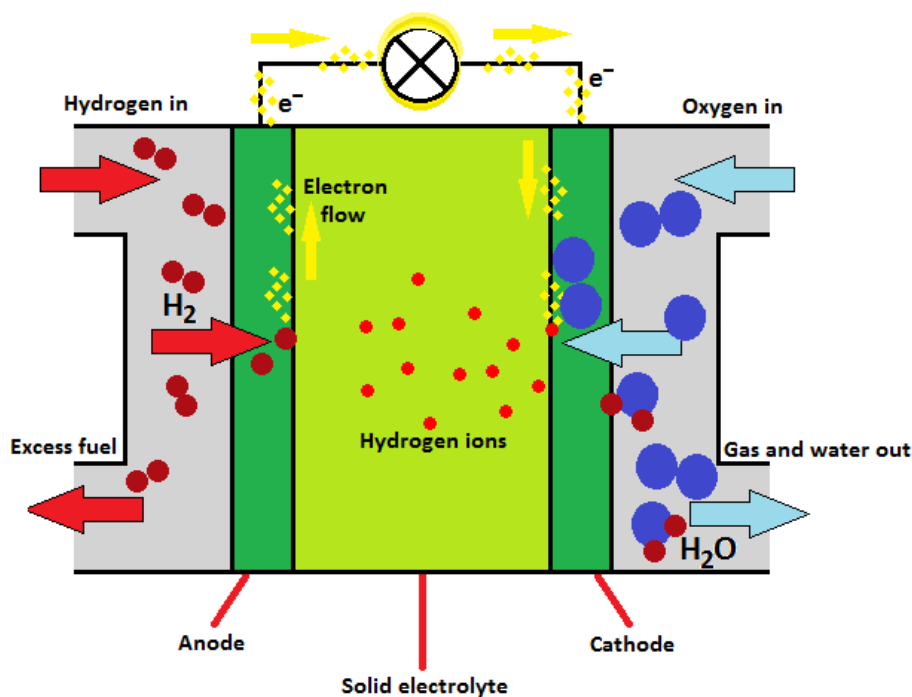


Figure 1. Fuel Cell schematic

If an appropriate fuel and oxidant are supplied (in this case hydrogen and oxygen), following chemical reactions take place:

Anode reaction: $2H_{2(g)} \rightarrow 4H^+ + 4e^-$

Cathode reaction: $O_{2(g)} + 4e^- \rightarrow 2O^{2-}$

Overall reaction $2O^{2-} + 4H^+ \rightarrow 2H_2O$

There are many different kinds of the fuel cells, which vary with type of supplied fuel, type of electrodes (typical, single layer) and electrolytes (liquid, solid) [6]. In the case of Protonic Ceramic Fuel Cell cathodes consist of mixed proton-electron or triple (proton, oxygen ion and electron) conducting polycrystalline materials [7]. The electrolyte most commonly used are proton conducting ceramics [8] and the anode is mixed proton-electron conductor [9].

3. HYDROGEN TRANSPORT IN PCFC

PCFC performance strongly depends on the hydrogen ions transport mechanism in the electrodes and electrolyte. Therefore, nature of this transport is of interest in the scientific community. The mechanism of proton conduction is still not entirely understood. Hydrogen ions H^+ are protons, which cannot exist separately in the crystal structure. Because proton has the highest charge density among all known ions in the periodic table, H^+ is highly affected by the Coulomb force. Therefore, in oxides, protons form bonds with oxygen ions and exist in the crystal structure as OH^- groups called 'protonic defect'. Scientists postulate two possible conduction mechanisms of these. One of them is called vehicle mechanism, in which proton is moving together with bigger ion, atom or molecule (in this case oxygen ion). It is illustrated in **Fig.2**. The second one is called Grotthus mechanism and in this mechanism, oxygen ion does not move in the crystal structure, whereas proton can be transported between oxygen ion positions. The movement is a two-step process. First, the O-H bond is rotating and in the second step, H^+ jumps to another oxygen ion. Because of the jumps present in this process, the mechanism is also called hopping mechanism and it is depicted in **Fig.3**. [10]



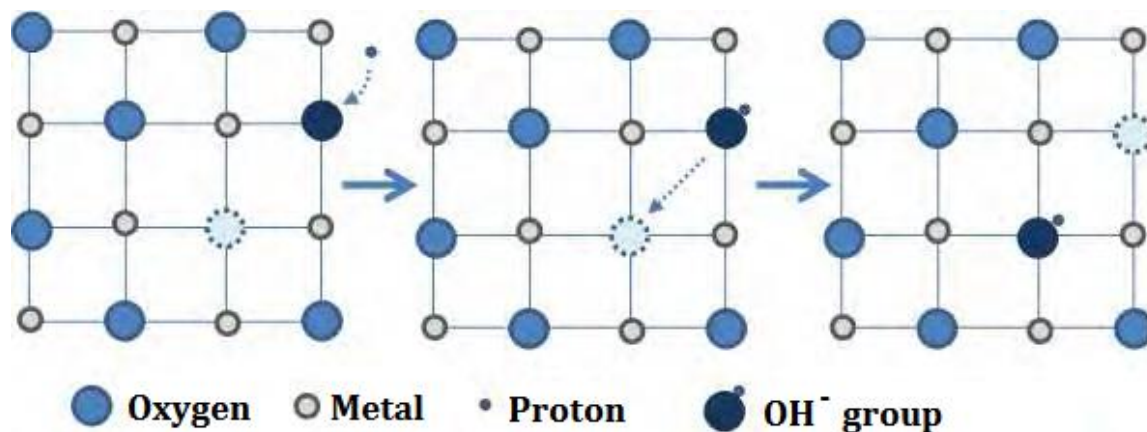


Figure 2. Schematic of vehicle mechanism. [10]

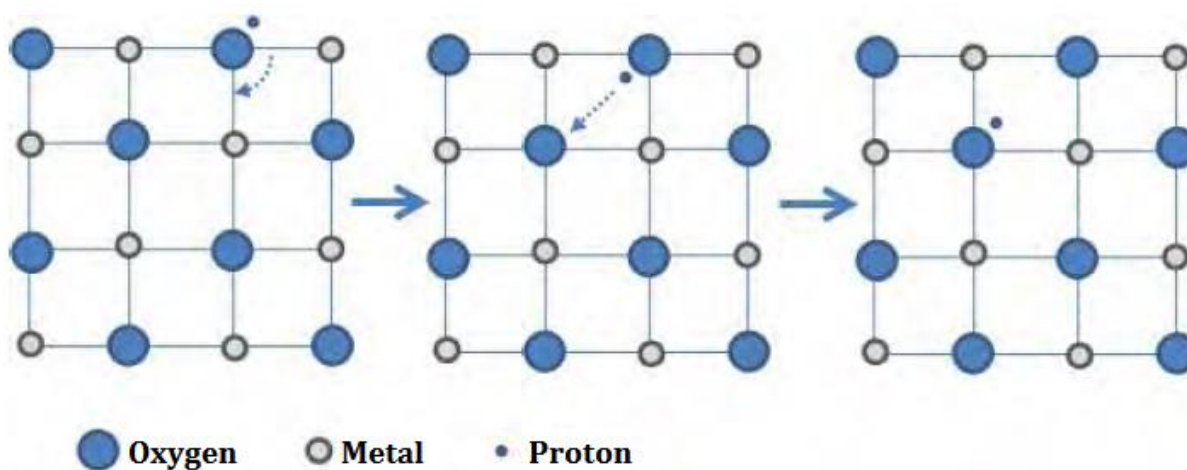


Figure 3. Schematic of the Grotthus mechanism. [10]

4. MATERIALS FOR PCFCs

Last decades were focused on finding novel materials for the electrodes and electrolytes for PCFCs [11]. The most common materials for an electrolyte are yttrium doped barium cerate, and yttrium doped barium zirconate (BCY and BZY, respectively). They exhibit the highest proton conductivity among perovskite type material [12, 13]. Sneha et al. showed that the proton conduction in BCY occurs by means of the defect equilibrium reactions between the oxygen vacancies, holes, lattice oxygen and water vapor at elevated temperatures [14]. Bae et al. showed that BCY/BZY electrolyte cell was much more stable under negative voltage operations than BCY, thus local electronic conduction, as well as chemical stability, can be

achieved by utilization of a BZY layer on the cathode side [15]. Another group of materials which have been extensively investigated for several years is rare earth niobates. They could be applied as an electrolyte in PCFCs. These compounds have chemical formula RENbO_4 [16] or RE_3NbO_7 , where RE is a rare-earth metal (for example, lanthanum, yttrium, gadolinium...). Lanthanum orthoniobate LaNbO_4 is a material which also can be used as an electrolyte. It exhibits proton conduction in wet atmospheres [17]. In temperature around $520\text{ }^\circ\text{C}$ phase transformation from monoclinic to tetragonal occurs [18]. Schematic representation of this transformation is shown in **Fig. 4** [19]

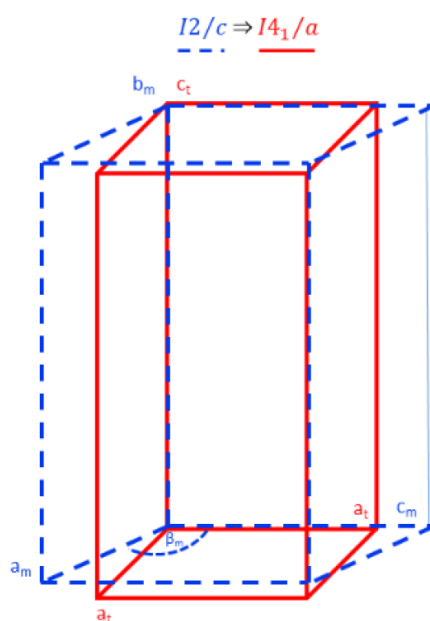


Figure 4 Phase transition from monoclinic to tetragonal in LaNbO_4 [19]

Ca or Sr doping at the A site (in ABO_4 system) introduces oxygen vacancies and thereby improves the electrical conductivity - a proton conductivity is close to 0.001 S/cm under $2.5\% \text{ H}_2\text{O}$ at $\sim 950\text{ }^\circ\text{C}$ [20]. Another group of rare earth niobates is RE_3NbO_7 which is interesting from the structural point of view. Depending on the rare earth metal radius, these compounds crystallize in defect fluorite type structure with various symmetry systems. This dependence is shown in **Fig.5**



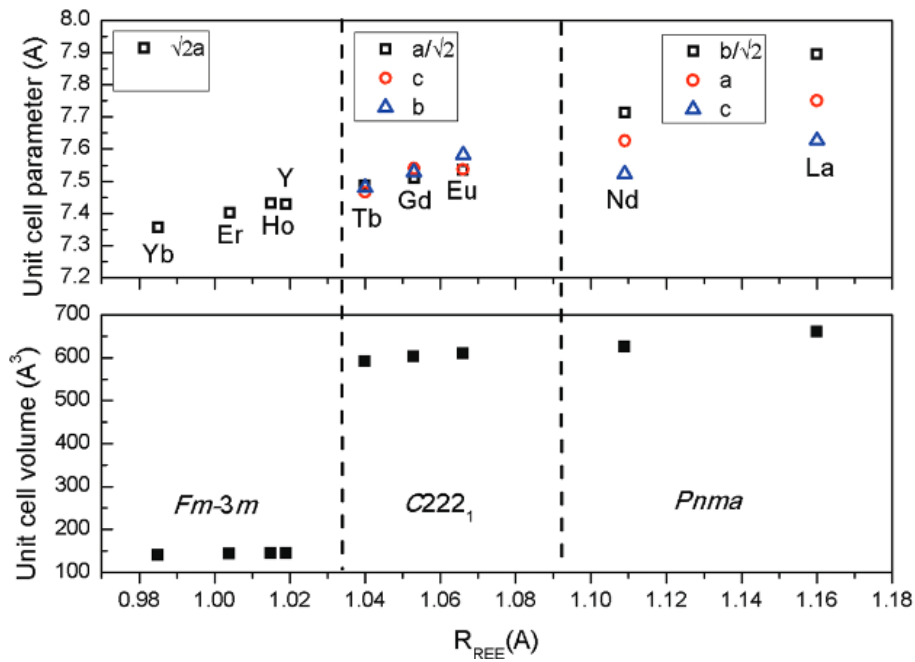


Figure 5 Ionic radius dependence of space group [21]

Y_3NbO_7 crystalizes in defect fluorite type structure with $Fm\bar{3}m$ space group. This material has oxygen vacancies in the crystal structure [22] – **Fig.6**. If these vacancies are filled with water vapor, the OH^- defects are forming which enhances the total conductivity of the material, with protonic conductivity incorporation [23]. It can be assumed that then Grotthus mechanism of transport takes place.

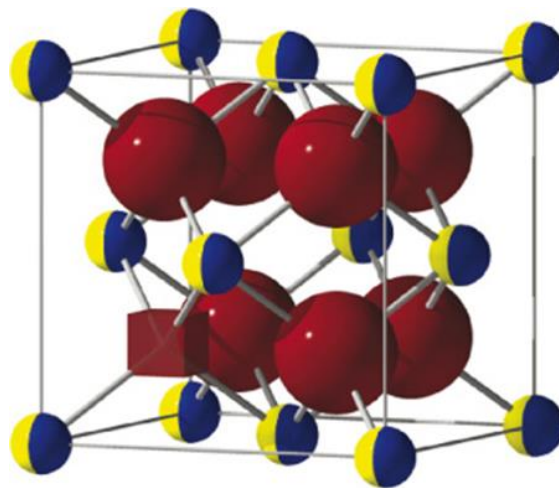


Figure 6. Defect fluorite type structure. Yellow/blue hemispheres = Nb/Y, red spheres = oxygen, red cube = oxygen vacancy. [24]

Materials for electrodes should exhibit good thermomechanical compatibility with the used electrolyte, excellent electrochemical activity for fuel oxidation at low temperature and high

electronic and ionic conductivity. Such properties are achievable in cermet electrodes, a composite material composed of ceramic (cer) and metallic (met) materials. This kind of materials are commonly used in the case of an oxygen ion conducting SOFCs. The most common anodes for the cells with the yttria-stabilized zirconia (YSZ) electrolyte are Ni-YSZ cermets but also e.g. $\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}-\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ cermet anode was reported by Chen et al. [25]. A similar approach may be used in the case of PCSOFCs. For example, Taillades et al. used Ni-BaCe_{0.9}Y_{0.1}O₃ (Ni-BCY) as cermet for the anode [26]. Also Li et al. reported cells, consisting of a Ni-BZCY anode, a 20 μm BZCY electrolyte, and a ~20 μm La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF) and Y_{0.25}Bi_{0.75}O_{1.5} (YSB) infiltrated LSCF cathode [27]. Their electrical tests were performed at 550 °C using humidified hydrogen as the fuel and ambient air as the oxidant. They showed that introducing 40 wt% of YSB influenced current density, which increased from 46 mW/cm² to 167 mW/cm².

In the last few years a number of studies have been focused on triple conducting oxides, which have mixed e⁻/O²⁻/H⁺ conducting properties [28]. A key obstacle to the practical operation of protonic ceramic fuel cells (PCFCs) is the development of high efficient cathode materials. Li et al. reported triple phase conducting composite consisting of Gd_{0.1}Ce_{0.9}O_{2-δ} (GDC) infiltrated PrBaCo₂O_{5+δ} (PBC) - (BZCY) materials as the novel cathode of PCFCs [29].

3. SUMMARY

The electrical energy market is changing rapidly due to depletion of fossil fuels deposits. Scientists are trying to find new sources of energy. One of them are the fuel cells, which produce electrical energy through simple chemical reactions. A novel Protonic Ceramic Fuel Cells are investigated. These devices have few major advantages: produces electrical energy through simple reactions, operates at lower temperatures (in opposition to Solid Oxide Fuel Cells), and are environmentally friendly. Scientists are presenting modern materials which could be used as electrodes or electrolytes in such fuel cells. Exhausting gas coming from a chemical reaction is typically water vapor, thus no waste is released to the atmosphere.

References

- ¹ M. Bando, *Urząd Regulacji Energetyki 2016*, (2016) 20-52.
- ² M. Guarnieri, *IEEE Industrial Electronics Magazine*, 8(3), (2014),
- ³ M. Gazda, P. Jasinski, B. Kusz, B. Bochentyn, K. Gdula-Kasica, T. Lendze, W. Lewandowska-Iwaniak, A. Mielewczyk-Gryn, S. Molin, *Diffusion and Defect Data-Solid State Data-Part B-Solid State Phenomena*, 1567(183), (2011)
- ⁴ Intelligent Energy. In: <http://www.intelligent-energy.com/technology/technology-faq/>
- ⁵ J.M. Andu'jar, F. Segura, *Renewable and Sustainable Energy Reviews* 13 (2009) 2309–2322
- ⁶ N.A. Baharuddin, A. Muchtar, M. R. Somalu, *International journal of hydrogen energy* 42 (2017) 9149 – 9155
- ⁷ L. Fan, P.C. Su, *Journal of Power Sources* 306 (2016) 369 377
- ⁸ Y. Li, L.M. Wong, H. Xie, S. Wang, P.C. Su, *Journal of Power Sources* 340 (2017) 98-103
- ⁹ Z. Tao, G. Hou, N. Xu, Q. Zhang, H. Ding, *Electrochimica Acta* 150 (2014) 55–61
- ¹⁰ A. Mielewczyk – Gryń, PhD Thesis, Gdańsk University of Technology, (2013)
- ¹¹ K. Zagórski, S. Wachowski, D. Szymczewska, A. Mielewczyk-Gryń, P. Jasiński, M. Gazda, *Journal of Power Sources*, 353(2017)
- ¹² I. Kalaitzidou, A. Katsaounis, T. Norby, C.G. Vayenas, *Journal of Catalysis* 331 (2015) 98–109
- ¹³ M.G. Jung, Y.J. Kim, Y.G. Jung, H.T. Lim, *International journal of hydrogen energy* 39 (2014) 16576 -16584
- ¹⁴ B.R. Sneha, V. Thangadurai, *Journal of Solid State Chemistry* 180 (2007) 2661–2669
- ¹⁵ S.Y. Baea, J.Y. Park, H.T. Lima, *Electrochimica Acta* 236 (2017) 399–407
- ¹⁶ T. Norby, A. Magraso, *Journal of Power Sources* 282 (2015) 28-33
- ¹⁷ Y. Cao, N. Duan, D. Yan, B. Chi, J. Pu, L. Jian, *International journal of hydrogen energy* 41 (2016) 20633-20639
- ¹⁸ Y. Cao, Y. Tan, D. Yan, B. Chi, J. Pu, L. Jian, *Solid State Ionics* 278 (2015) 152–156
- ¹⁹ S. Wachowski, PhD Thesis, Gdansk University of Technology, 2016
- ²⁰ A. Magrasó, M.L. Fontaine, R. Bredesen, R. Haugsrud, T. Norby, *Solid State Ionics* 262 (2014) 382–387
- ²¹ A. Mielewczyk-Gryń, A. Navrotsky, *American Mineralogist*, Vol. 100, Issue 7, 2015
- ²² M. Wakeshima, Y. Hinatsu, *Journal of Solid State Chemistry* 183 (2010) 2681–2688
- ²³ A. Chesnaud, M.-D. Braidia, S. Estradé, F. Peiró, A. Tarancón, A. Morata, G. Dezanneau, *Journal of the European Ceramic Society* 35 (2015) 3051–3061
- ²⁴ K.E. Sickafus, R.W. Grimes, J.A. Valdez, A. Cleave, M. Tang, M. Ishimaru, S.M. Corish, C.R. Stanek & B.P. Uberuaga, *Nature Materials*, 6 (2007), 217 - 223
- ²⁵ Y. Chen, Z. Cheng, Y. Yang, W. Yu, D. Tian, X. Lu, Y. Ding, B. Lin, *Materials Letters* 188 (2017) 413–416
- ²⁶ G. Taillades, P. Batocchi, A. Essoumhi, M. Taillades, D.J. Jones, J. Rozière, *Microporous and Mesoporous Materials* 145 (2011) 26–31
- ²⁷ G. Li, B. He, Y. Ling, J. Xu, Ling Zhao, *International journal of hydrogen energy* 40 (2015) 13576 -13582
- ²⁸ Q. Jiang, J. Cheng, R. Wang, Y. Fan, J. Gao, *Journal of Power Sources* 206 (2012) 47–52
- ²⁹ G. Li, Y. Zhang, Y. Ling, B. He, J. Xu, L. Zhao, *International journal of hydrogen energy* 41 (2016) 5074-5083

