WEB ISSN 2535-0013
PRINT ISSN 2535-0005

REVERSIBILITY IN AN INNOVATIVE DUAL MEMBRANE FUEL CELL DESIGN

Prof. D.Sc. Vladikova D.[1], Prof. D.Sc. Stoynov Z. [1], Dr. Burdin B. [1], Assoc. Prof. Raikova G. [1],
Dr. Krapchanska M. [1], Prof. Thorel A. [2], Dr. Chesnaud A. [2]
Institute for Electrochemistry and Energy Systems - BAS, Sofia, Bulgaria 1
Centre des Matériaux, MINES-ParisTech, PSL, UMR CNRS 7633 BP 87, France 2

d.vladikova@iees.bas.bg

Abstract: *A promising direction in the development of solid oxide fuel cells (SOFCs) is the reversible approach in which the device operates as fuel cell, producing electricity and heat, and as electrolyzer producing the hydrogen fuel. Reversibility strongly increases the device efficiency. It is very convenient for coupling with Renewable Energy Sources and for off grid applications. Although being very important, this direction of SOFC development still needs serious research efforts for the increase of durability, performances and efficiency and decrease of the switching time. A definitive breakthrough is the separation of the water production/consumption from the two electrodes. This work presents systematic studies on a new design of SOFC with a separate compartment for water formation in fuel cell mode and water injection in electrolyzer mode, named monolithic dual membrane fuel cell. It is based on the discovered property of some proton conducting ceramics to behave as mixed ionic conductors. The first tests of laboratory cells show promising performance with excellent reversibility which opens a pathway for further developments on higher technology readiness level.*

Keywords: SOLID OXIDE FUEL CELL, DUAL MEMBRANE FUEL CELL, PROTON CONDUCTIVITY, MIXED IONIC CONDUCTIVITY, REVERSIBLE MODE, ELECTROLYZER, SEPARATE WATER COMPARTMENT

1. Introduction

Fuel cells and Hydrogen are of key importance for the successful transformation to low carbon economy which makes them essential part of the technologies included in the European Strategic Plan for Energy Technologies (SET Plan) [1]. The SET plan emphasizes on generating green electricity by the development of affordable and integrated energy storage solutions from renewable energy sources (RES) which is the backbone of the sustainable energy model. The report of the International Energy Association from January 2013 stressed on the importance of hydrogen as energy carrier produced from water with electricity from RES, and converted again in electricity and heat when necessary with fuel cells. The whole process ensures zero emissions.

Solid Oxide Fuel Cells (SOFC) are electrochemical devices that convert fuel chemical energy (most often hydrogen) into electricity at high temperature. Since they present high efficiency and large fuel flexibility, SOFCs appear as an attractive technology for economic power generation. The active part of SOFC corresponds to a three-layered structure, constituted by a dense oxide ion conducting electrolyte sandwiched between two porous electrodes. SOFC have the greatest potential for combined heat and power generation in stationary conditions. The development of proton conducting solid oxide fuel cells (pSOFC) has started more than 20 years ago, when the phenomenon of proton conductivity has been found in some Y-dopped cerates with perovskite structure. The main advantage of that design is that the water does not dilute the fuel, as it is in the classical SOFC, while the production of strongly corrosive water due to its contact with the oxidizer can be regarded as a serious disadvantage.

Resent investigations show that high temperature solid oxide electrolyzers (SOEC) have a number of advantages in respect to the alkaline and proton conducting electrolyzers [2-7]. A new direction is the development of electrolytes based on proton-conducting ceramics (pSOEL). With fast developments of renewable electricity production, the issue of storing surplus electricity in periods of high production has gained a new dimension on-grid, as well as off-grid. Often conventional grid control mechanisms are overloaded, with the result being that power plants have to shut down more frequently. Batteries and pumped water storages can address short-term storage, but they require repetitive charging and discharging cycles and are therefore limited in their storage capacity. The concept idea of Power-to-Gas (PtG) promises a possible solution for large scale and long-term storage.

The idea for fuel cell operation in reversible regime is relatively new in global aspect, but with quickly increasing importance due to the expected impact from coupling with RES. The reversibility of Solid Oxide Cells allows electricity production at high electrical efficiency from H_2 using the same device in times of power shortages. Unlike batteries, the reversible solid oxide cells (rSOC) storage capacity can be increased by adding storage tanks or connecting the system to the natural gas grid, instead of increasing the converter. To improve state of the art rSOC in direction cost-efficient, industrial range, their design has to be improved. Although the construction of SOECs and SOFCs looks similar, there is no optimized application of reversible high temperature electrochemical device due to their asymmetry which causes big differences in the operating conditions. For instance the high current density associated with a large amount of water in the fuel electrode for SOECs compared to SOFCs strongly increases the polarization resistance, the constraints on interconnects and the overall degradation rate. Durability, performances and efficiency of SOECs are affected by: accelerated degradation and delamination at the hydrogen or the air electrode due to the presence of water; high temperature and current flow; slow and difficult switching form mode to mode; high humidity of the produced H_2; difficulties in cell pressurization [2, 8-10]. Studies point out the negative effect of water vapor on interconnect durability both in a reducing and oxidizing environment (related to Cr diffusion/evaporation), which renders the presence of a coating to protect interconnects mandatory [3,5].

This work is dedicated to the development of a new design of solid oxide fuel cell which can work as reversible fuel cell answering the demands for fast reversibility. It is based on a new design of fuel cell, named “dual membrane fuel cell” (dmFC), proved in the frames of an 7 FP FET project [11,12]. The new architecture eliminates the problems coming from the water formation and evacuation from the electrodes [13-15].

The kernel of the new concept is a fuel cell with 3 compartments. The assembly combines the cathode compartment (cathode/electrolyte) of a SOFC and the anode compartment (anode/electrolyte) of pSOFC sandwiching a porous central membrane with mixed proton and oxide ion conducting ceramic structure, where the water is produced and evacuated. This leads to numerous advantages (lower electrodes overpotential, easy pressurization, no dilution of fuel or oxidant). Since water is the major source of SOFC and SOEC failure, the long term viability of this concept should be significantly enhanced. The separation of the water in a special compartment where it is formed (in FCFC mode), or injected (in SOEC mode), and thus the elimination of its

WEB ISSN 2535-0013
PRINT ISSN 2535-0005

damaging presence at the electrodes in both modes, combined with the reduced operating temperature from 800-950°C to 600-800°C, are strong logical arguments in favor of the hypothesis for advanced reversible electrochemical device based on the dmFC design. A unique advantage is the flexibility of operation, i.e. the quick change of mode due to the presence of strongly adsorbed water in the corresponding chamber. Additionally a mixed ionic conductivity in the proton conducting electrolyte (BCY15) was registered and preliminary experiments were performed on the so called "monolithic design". in which only one type of electrolyte with mixed ionic conductivity can be used. This modification strongly simplifies the technology [13, 15]. In addition a new phenomenon is under fundamental studies - the presence of highly polarizable nanometer film of "organized" water at the surface of the BCY15 pores [16]. It should facilitate the water formation/splitting which supports the direction of research towards reversibility [14,15].

This work aims at a deeper insight into the phenomena occurring in a new monolithic design of a dual membrane fuel cell for the development of a next generation of reversible cell.

2. Experimental

The new component which ensures the advantages of the dmFC is the water chamber, named Central Membrane (CM). It is a principally new component of the fuel cell which should ensure several functions which contradictory initial requirements: on the one hand the CM should have high mixed ion conductivity, which is favored by a dense (usually composite) microstructure. On the other hand it plays a role of a chemical reactor where water is formed or injected, which needs a porous microstructure. For the optimization of the microstructure a new design of an experimental half cell representing the CM was systematically investigated applying a combination of several experimental techniques: (i) impedance spectroscopy which should give information about the mixed conductivity at different temperatures and microstructure; (ii) microstructural, combined with measurements of gases permeability in porous membrane. Usually the applied characteristic parameter is the mean value of porosity which may be obtained applying different techniques and methods as SEM/EDXS, mercury or Archimedes porometry, BET. However, samples with one and the same mean porosity may have different permeability depending on the geometry and tortuosity [1]. For more accurate characterization of the microstructure in the last years X-ray micro-tomography with 3D image analysis is applied. Although very precise, the method cannot be used for running lab optimization experiments since it is time consuming and expensive and needs synchrotron radiation [17].

For the performance of the permeability studies simple testing system was specially designed for measurements of the pressure P (mm H_2O) as a function of the gas flow q_{flow} [ml/min] penetrating through samples with different porosity. A new characteristic parameter, named permeability resistance R_p (inversely proportional to the permeability), was introduced:

$$R_p = P / q_{flow} \quad (1)$$

The testing system ensures measurements of P up to 5000 mm mm H_2O. The permeability measurements were carried out with different gases: air, H_2, O_2, N_2 and their mixtures. Gas humidity (3% H_2O) was ensured by passing the gas flow through watered vessel at room temperature. The experiments were carried out on samples with different porosity, evaluated by mercury porometry.

Similarly to the ohmic resistance, the permeability resistance has been expressed as:

$$R_p = \rho_p hs \quad , \quad (2)$$

where "s" is the sample's surface and "h" is its thickness.

Studies on barium cerate based materials have proved their high proton conductivity as a result of a loosely packed structure, combined with high basicity which decreases the chemical stability in acidic gases [18, 19]. In addition the dual membrane cell is developed to work with hydrogen fuel, which bypasses the problems arising from the presence of acidic gases [20]. Since the reactivity of barium cerates towards water vapor decreases at higher temperatures, it was supposed that at operating temperatures (600-800^oC) the stability of the material would not present a significant problem for the performance [20, 21], which was experimentally confirmed [22]. Thus the selected material was $BaCe_{0.85}Y_{0.15}O_{2.925}$ (BCY15). For optimization studies of the CM, samples with diameter about 2 cm and thickness about 1 mm were produced by cold pressing and sintering at 1300^oC. Different porosity (5 – 50 v %) was obtained by applying different quantities of graphite as pore former. The conductivity studies of BCY15 were performed by impedance spectroscopy measurements on symmetrical half-cells $Pt/BCY15_{porous}/Pt$ in temperature range room - 700^oC in both oxygen and hydrogen with 3 v % water.

For experimental proof of the reversibility in monolithic type button cells a three layered structure of BCY15: electrolyte/porous CM/electrolyte ($BCY15_{dense}/BCY15_{porous}/BCY15_{dense}$) with diameter about 22 mm and thickness of 1 to 2 mm was prepared by single stage cold pressing and sintering at 1300°C for 5 hours. The porosity of the CM was ensured by applying graphite pore former for the internal CM layer. The button cell was fabricated by deposition of platinum electrodes. The electrochemical measurements were performed in oxygen on the cathode side and nitrogen/hydrogen blend on the anode side. In electrolyzer mode the water produced in the CM was used.

The impedance measurements were performed on IVIUM - CompactStat e10030 in the frequency range 1 MHz – 0,01Hz and temperature interval 100^oC - 800^oC. The amplitude of the AC signal varied in the range 200 – 10 mV, depending on the resistance which decreases with the temperature.

3. Results and discussion

BCY15 is a good proton conductor [18, 19]. Under humidified hydrogen atmosphere protonic defects are formed by dissociative absorption of water in the presence of oxygen vacancies. Water vapor dissociates into a hydroxide ion which fills an oxide-ion vacancy, and a proton that forms a covalent bond with lattice oxygen, i.e. two proton defects are created stoichiometrically:

$$2OH^{\bullet} \leftrightarrow H_2O_{(g)} + V_O^{\bullet\bullet} + O_O^x \quad (3)$$

However, the presence of oxide-ion vacancies could be regarded as a precondition for oxide ion conductivity. There is some information about observed dual ionic conductivity in the system $BaCe_{1-x}Y_xO_3$ at higher substitution levels. No data for BCY15 were found. Our preliminary impedance measurements of BCY15 in hydrogen and oxygen showed high proton and oxide ion conductivity at fuel cell operating temperatures. The result opened a pathway towards the development of the new "monolithic" generation of dmFC [15]. However, the utilization of this finding needs a methodological survey for optimization of the CM conductivity and permittivity in order to obtain an optimized in respect to the water formation/evacuation microstructure. For this purpose impedance measurements in dual atmosphere were performed on BCY15 samples with different porosity (Table 1).

Table 1. *Central membrane samples*

Sample No	Porosity [v %]
1	9
2	27
3	35
4	47

SEM images of their microstructure are presented in Fig. 1. The samples have homogeneous porous structure with mean diameter of about 2 μm with the exception of sample 1 which has higher density and bigger grain size (Fig. 1).

The impedance measurements of the samples in oxygen and hydrogen gave information about the samples resistance as a function of the temperature (Figs. 2, 3) which was used for the building of the Arrhenius plots (Figs. 4, 5), compared for every

WEB ISSN 2535-0013
PRINT ISSN 2535-0005

atmosphere. The obtained results show that BCY15 has good mixed ion conductivity at operating temperatures (about 700°C).

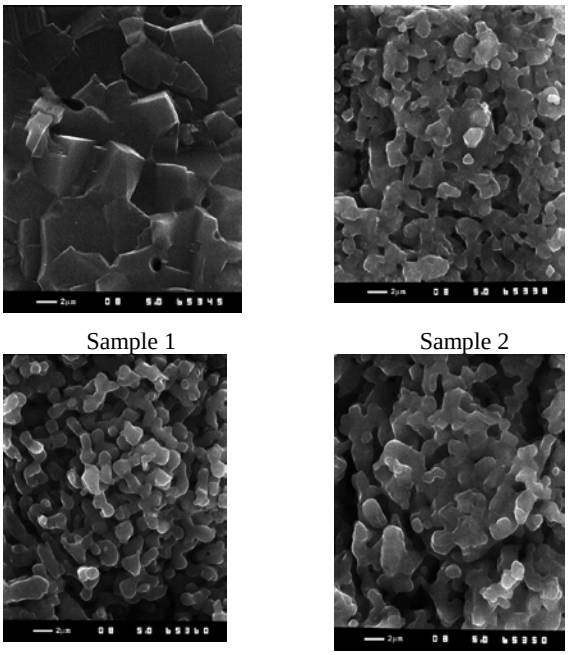

Fig. 1 *SEM images of central membrane samples with different porosity (given in Table 1)*

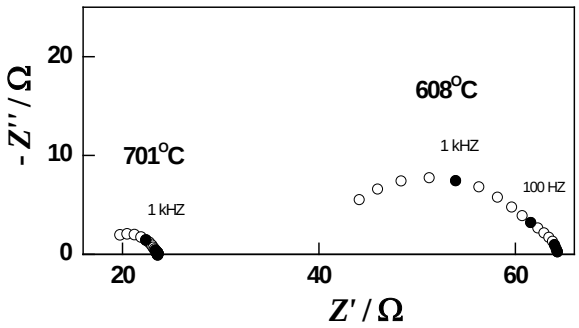

Fig. 2 *Impedance diagram of Sample 2 in oxygen*

Proton conductivity is less sensitive to the microstructure. It is interesting to note that at about 700°C the conductivities in the two atmospheres become similar, i.e. relatively independent on the porosity.

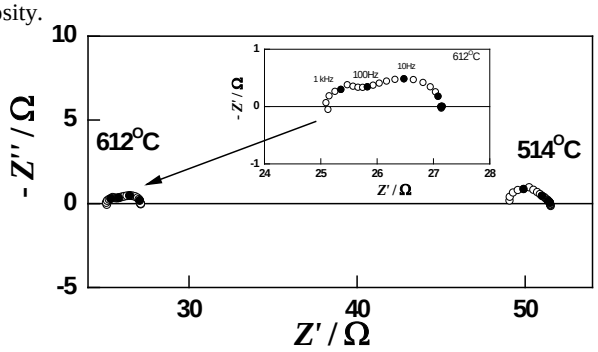

Fig. 3 *Impedance diagram of Sample 2 in hydrogen*

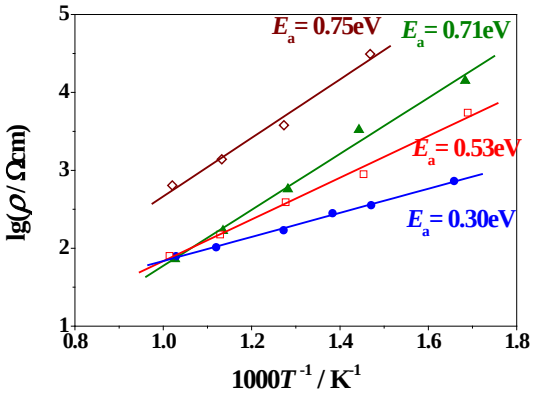

Fig. 4 *Arrhenius plots for the CM samples measured in oxygen: Sample 4 (◊); Sample 2 (▲); Sample 1 (□); Sample 3 (●)*

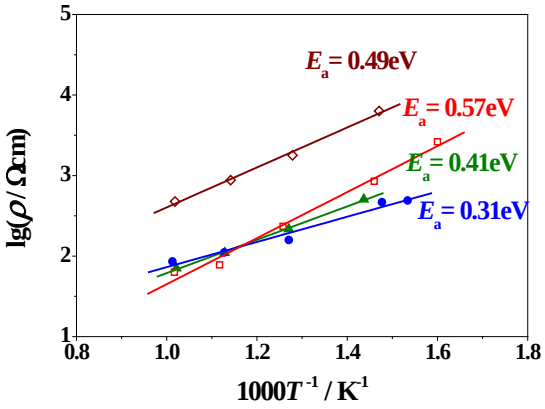

Fig. 5 *Arrhenius plots for the CM samples measured in humidified hydrogen: Sample 4 (◊); Sample 2 (▲); Sample 1 (□); Sample 3 (●)*

This result is very important, since it shows that the CM may have higher porosity combined with good conductivity, which in respect to the oxide ions is even higher than that of the standard oxide ion conductors.

For the evaluation of the porosity permeability, measurements with different gases were performed. A strong correlation was registered between the gas permeability and its molecular weight: the higher the molecular weight, the bigger the permeability resistance (Figs.6, 7). A linear dependence was observed for the investigated gases and their mixtures which may be used for prediction of the different gas mixtures permeability, which is very important for the usually applied N_2/H_2 blend at the anode side of the standard fuel cell (Fig.7).

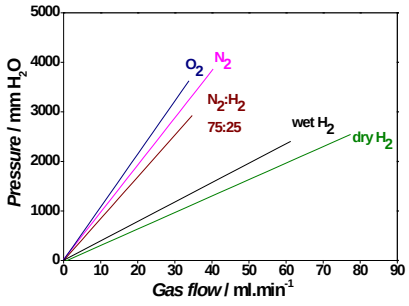

Fig. 6 *Dependence of the pressure from the gas flow for Sample 4*

WEB ISSN 2535-0013
PRINT ISSN 2535-0005

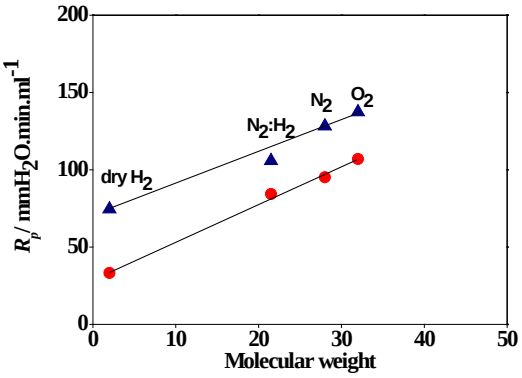

Fig. 7 *Permeability resistance as a function of the gas molecular weight for Sample 4 (●) and sample 1 (▲)*

The analysis of the obtained results shows that for the development of monolithic type dmFC a CM with porosity in the range 30-35% could ensure optimal conductivity, permeability and mechanical stability.

Fig. 8 presents the porous microstructure of the CM in contact with the dense electrolyte.

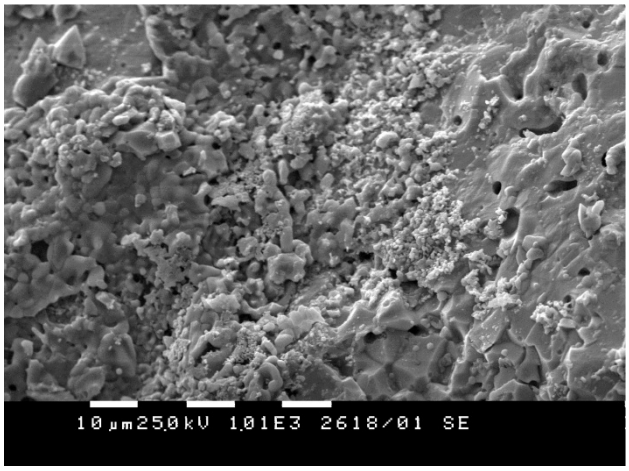

Fig. 8 *SEM image of porous Central Membrane and dense electrolyte, both from BCY15*

The first experiments on button cells with Pt electrodes show very promising results in reversible mode. The switch from fuel cell to electrolyzer mode demonstrates instantaneous reversibility. The volt-ampere curves illustrate better performance of the cell in electrolyzer mode (Fig. 9).

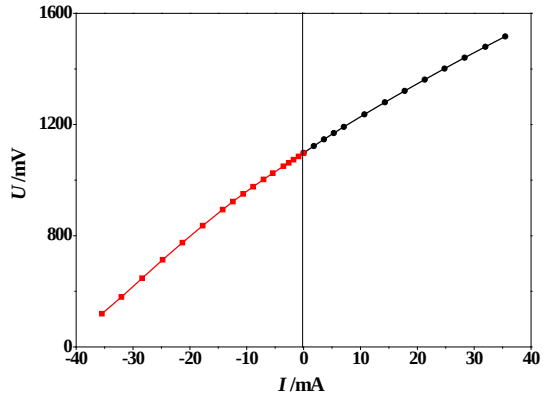

Fig. 9 *Volt-ampere characteristics of button cell measured in fuel cell and in electrolyzer mode at 700°C*

4. Conclusions

The systematic studies of the central membrane of monolithic dual membrane fuel cell which provides for separate formation/evacuation of water showed that 30-35% porosity could ensure an optimal microstructure in respect to conductivity, gas permeability and mechanical stability. The first tests of laboratory cells show promising performance with excellent reversibility which is encouraging for further development of the innovative reversible fuel cell design on higher technology readiness levels.

Acknowledgements

This work was supported by the Bulgarian National Science Fund under grant agreement E02/3/12.12.2014.

5. References

1. European Strategic Energy Technology plan http://ec.europa.eu/energy/technology/set_plan.
2. Abate C., M. Boaro, M. Ferluga, A. Pappacena, A. Trovarelli, European Fuel Cell Forum 2011, Chapter 14 - Session 805 - 11/56.
3. Stuart P.A., T. Uhno, J.A. Kilner, S.J. Skinner, Solid State Ionics 179 (2008) 1120.
4. Brisse A., J. Schefold, M. Zahid, International Journal of Hydrogen Energy 33 (2008) 5375.
5. Zaid M., A. Schefold, Brisse, Hydrogen and Fuel Cells, Fundamentals, Technologies and Aplications, Wiley-VCH, Weinheim, Germany, 2010, 227.
6. Hauch A., S.H. Jensen, M. Mogensen et al., J. Electroehem. Soc., 153 (9) (2006) 1741.
7. Jensen, S.H., P.H. Larsen, A. Hauch et al., Inter. J. Hydrogen Energy 32 (2007) 3253.
8. Lee Y., D. Y. Kim, G. M. Choi, Solid State Ionics 192 (2011) 521.
9. Yan L., H. Ding,Z. Zhu,X. Xue, J. Power Sources 196 (2011) 9352.
10. Guo Y., R. Ran, Z. Shao, International Journal of Hydrogen Energy 36 (2011) 1683.
11. wwrv.ideal-cell.eu
12. Patent No0550696000 March l7th, 2005 "Cellule de Pile a Combustible Haute Temperature a Conduction Mixte Anionique et Protonique" extended internationally in 2007, invented by the Centre des Materiaux d'Evry, common research center to ARMINES and MINES ParisTech.
13. Patent No 20120156573, 21.06.2012., "Fuel Cell with Monolithic Electrolytes Membrane Assembly", Thorel A., Z. Stoynov, D. Vladikova, A, Chesnaud, M. Viviani, S. Presto
14. Vladikova D.,Z. Stoynov, G. Raikova, A. Thorel, A. Chesnaud, J. Abreu, M. Viviani, A. Barbucci, S. Presto, P. Carpanese, Electrochimica Acta 56 (2011) 7955.
15. Vladikova D., Z. Stoynov, A. Chesnaud, A. Thorel, M. Vivianu, A. Barbucci, G. Raikova, P. Carpanese, M. Krapchanska, E. Mladenova, International Journal of Hydrogen Energy, 39(36) (2014) 21561.
16. Stoynov Z., D Vladikova, E. Mladenova, Journal of Solid State Electrochemistry, 17 (2013) 555-560, DOI 10.1007/s10008-012-1916-z.
17. William M. Harris, Jeffrey J. Lombardo, George J. Nelson, Barry Lai, Steve Wang, Joan Vila-Comamala, Mingfei Liu, Meilin Liu & Wilson K. S. Chiu, Scientific Reports 4, Article number: 5246 (2014),doi:10.1038/srep05246
18. Iwahara H., Solid State Ionics 86-88 (1996) 9.
19. Norby, T., Solid State Ionics 125 (1999) 1.
20. Coors W.G., J. Electrochem.Soc. 151 (2004) A994.
21. Coors W.G., Solid State Ionics178 (2007) 481.
22. Gawel, R. K. Przybylski, M. Viviani, J Therm Anal Calorim 2013: DOI 10.1007s/10973-01303562-9.