CATHODE FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELL (IT-SOFC)

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ABSTRACT

Solid oxide fuel cells (SOFC) directly convert fuel into electricity hence it received a great deal of interest as alternative high performance and environmentally friendly power generation systems. The high operating temperature limits technological development of solid oxide fuel cell. Intermediate temperature solid oxide fuel cells (IT-SOFCs) overcome these limitations because of its intermediate operating temperature. Reducing the operating temperature, however, decreases the cathode kinetics resulting in the large interfacial polarization resistances. Perovskite and related oxides are extensively explored for applications in IT-SOFC electrodes. Recently, K_2NiF_4-type structure materials are investigated for cathode materials as they exhibit oxygen over-stoichiometry.

Keywords: *SOFC, IT-SOFC, Cathode, Perovskite Materials, MIEC, K_2NiF_4.*

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Introduction

Fuel cells are the electrochemical power source, which directly convert fuel into electricity without the need for combustion. Hence, they received a great deal of interest as alternative high performance and environmentally friendly power generation systems. Low temperature fuel cells viz; polymer electrolyte membrane fuel cells (PEMFCs), alkali fuel cells (AFCs) and phosphoric acid fuel cells (PAFCs) are appropriate for small-scale applications, such as laptops, cellular phones, and automobiles. In contrast, high temperature fuel cells, such as molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs), are suitable for large-scale power plants and distributed power. In this regard the major advantages include relatively higher efficiencies, greater fuel flexibility, and the possibility of combined heat and power generation. Among several types of fuel cells, SOFCs are considered to be the most apt fuel cell for generating electricity in stationary applications due to their simplicity, fuel flexibility, high-performance, solid-state material (easy to handle), and possibility for insitu hydrocarbon reforming [1-13].

Nowadays, however, the technological developments on solid oxide fuel cells (SOFC) are limited due to their high operating temperatures, typically around 800 – 1000 °C. In this temperature

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range, low-cost interconnect materials are not useful, and long-term stability of the cell cannot be ensured as chemical reactions occur between electrodes and electrolyte [14]. In recent years, great efforts are directed to develop intermediate temperature SOFCs (IT-SOFCs) operating in the range 500–800 °C. Lowering operating temperature can suppress degradation of components and extend the range of acceptable materials selection; this, also, improves cell durability and reduces the system cost. Reducing the operating temperature, however, decreases the electrode kinetics resulting in the large interfacial polarization resistances. This effect is most significant for the oxygen reduction reaction (ORR) at the cathode [15]. The cathode, thus, must exhibit following properties [16]:

- High electronic conductivity (preferably more than 100 S cm^{-1} under oxidizing atmosphere)

- Thermal expansion coefficient (TEC)compatible with electrolyte

- Chemical stability with the electrolyte and interconnect materials

- Adequate porosity to allow gaseous oxygen to readily diffuse through the cathode to the cathode/electrolyte interface

- Thermodynamically stable under an oxidizing atmosphere during fabrication and operation

- High catalytic activity for the oxygen reduction reaction (ORR)

- Low-cost.

Development of Cathode Materials

Tedmon et al. on the basis of extensive literature survey concluded that the cathode materials developed during 1960s for high temperature zirconia electrolyte fuel cells are still incompatible [17]. The high operating temperature of the of solid oxide fuel cells (SOFCs) invites the use of only noble metals or electronic conducting oxides as cathode materials. However, electrodes based on noble metals are rejected due to their high cost [17]. Although Ag exhibits many favorable characteristics, its relatively high vapor pressure even at 800°C,discarded this material due to the associated short lifetime predictions (<10.000h) [18].

Composite cathodes comprising zirconia electrolyte powder and noble metal current collectors exhibited good performance but again are not considered to be economically viable solution. Investigations with a variety of mixed conducting oxides such as $La_{0.9}Sr_{0.1}CoO_3$, $PrCoO_3$ and Pr_2CoO_4shown promising results but the initial performance degraded rapidly due to the formation of interfacial reaction products such as $SrZrO_3$ and $La_2Zr_2O_7$. Also, they exhibited lack of good adherence due to mismatch in TEC of the perovskite cobaltites with stabilised zirconia. More promising results are obtained with cathodes based on UO_2 solid solutions, but most commercial developers rejected these materials also due to their radioactivity [18].

In the early 1970s, the porous composite $La_{1-x}Sr_xMnO_3$-yttria stabilised zirconia (LSM-YSZ) electrode prima fuci is established as the most appropriate cathode to use with zirconia electrolyte in fuel cells [18]. Another 20 years elapsed before the demonstration of negligible oxygen flux through LSM, and the YSZ component must be responsible for a major contribution of oxygen supply to the composite electrolyte component [18]. The development of cathodes for ceria-based electrolytes had not seriously addressed until the early 1990s, with the development of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ materials. Until the introduction of these electrodes most investigators had used Pt cathodes [18].

As discussed earlier, the IT-SOFC are the promising fuel cells. The electrodes for IT-SOFC should have high electrical conductivities, adequate porosity for gas transport, good thermal and chemical compatibilities with the electrolyte for long-term stability. Performance is governed by the electronic resistivity of the electrode, overpotentials associated with charge-transfer at the electrode – electrolyte gas-phase boundaries (TPB), the ionic resistance of the electrolyte, and rate of transport of gases through the porous electrodes [19].

Recently, a good number of oxides are projected as potential cathode for SOFC applications having improved electrochemical performance at relatively lower temperatures and resistant to degradation during operation [14, 20]. Practically, perovskite and related oxides are extensively explored for a range of applications including IT-SOFC/ SOFC electrodes and high temperature superconductors [20-26].
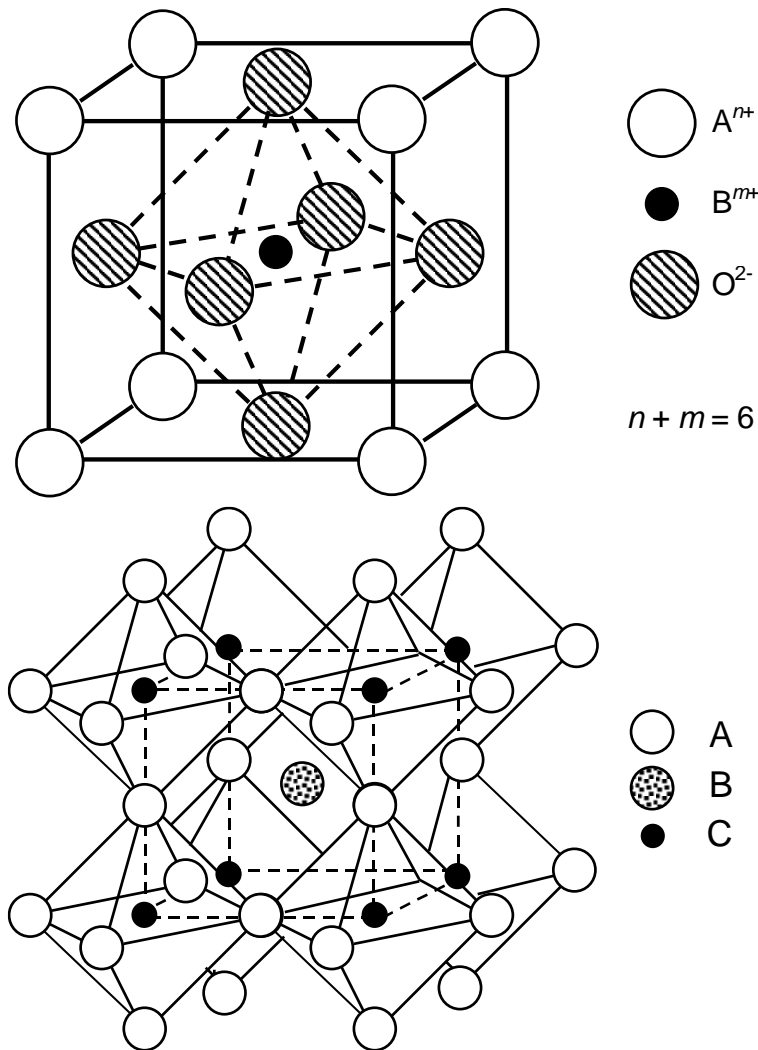
Perovskite Cathode Materials

Fig. 1: (a) Unit cell of the ABO₃ perovskite structure [29] and (b) Schematic of cubic perovskite structure [16, 30]

Perovskite materials are widely used as cathode in SOFCs [27]. The fundamentals of the perovskite structure are necessary for better design and optimization of the cathode materials. A perovskite-type oxide are of general formula ABO_3, in which A and B are cations with a total charge of +6. The lower valence A cations (such as, La, Sr, Ca, and Pb, *etc.*) are large and coordinated to twelve oxygen anions. The B cations (such as, Ti, Cr, Ni, Fe, Co, and Zr, *etc.*) occupy the much smaller space and are coordinated to six oxygen anions. Full or partial substitution of A or B cations with cations of different valence is possible. When the overall valence of the A-site and B-site cations ($n + m$) adds up to less than six, introduces vacancies at the oxygen lattice sites to achieve charge neutrality [28, 29]. The typical crystal structure of the ABO_3 cubic perovskite is depicted in Figs.1(a) [29] and (b)[30]. Many perovskite structures are distorted and do not have cubic symmetry. Common distortions, in these materials, viz cation displacements within the octahedra and tilting of the octahedra are co-related to the properties of the A and B atoms. The degree of distortion in ABO_3 perovskites can be determined according to the Goldschmidt tolerance factor (t):

$$t = \frac{(r_A + r_B)}{\sqrt{2}(r_B + r_O)} \tag{1}$$

where $r_A, r_B,$ and r_O are the effective ionic radii of *A, B*, and O ions, respectively. In general, *t* is evaluated using pertinent Shannon's ionic radii [31].Nearly unity tolerance factor implies ideal cubic structure. Smaller *A* or bigger *B* cations leads to a decrease in tolerance factor causing cation displacement and tilting of corner sharing BO_6 octahedra which results in orthorhombic symmetry [32]. For most of the perovskite materials used as cathodes in SOFCs, the *A*-site cation are the mixture of rare and alkaline earths (La and Sr, Ca or Ba), while the *B*-site cation are the reducible transition metal such as Mn, Fe, Co, or Ni (or a mixture thereof). In most of the cases, a redox catalytic mechanism is, thus, generally is due to *B*-site cations [33]. The octahedral symmetry around the transition metal is invariably responsible for a metallic or semiconducting band structure at high temperatures, concurrently high electronic conduction. With a rational selection of *A*- and *B*-site cations, a large number of thermodynamically stable oxygen ion vacancies can be introduced at SOFC's operating conditions. Such vacancies facilitated high bulk ionic oxygen transport [34].

The oxygen vacancies in $Ln^{3+}_{1-x}Sr^{2+}_xM^{3+}O_{3-\delta}$ can be created either by the partial substitution of A^{3+} by A^{2+} or due to the partial reduction of B^{3+} or B^{4+} to B^{2+} and B^{3+}, respectively [35, 36]. Oxygen mobility through vacancies is the basis for oxide ion conductivity. In some compositions of perovskite-type oxides, the oxide ion conductivities are as high as those observed in solid electrolyte, *e.g.*, the ionic conductivity of $Sr_{0.9}Ce_{0.1}CoO_{3-\delta}$ reaches 0.133 S cm^{-1} at 800 °C in air [37-39]. The improved electrical conductivity and electrocatalytic performance in most cathode materials rely on doping of both the *A*- and *B*-sites. Over and above the electrical and the structural characteristics mentioned above, thermodynamic data are also essential for evaluating the long-term stability of perovskite cathode materials, and establish their compatibility with other components at SOFC operating temperatures. Yokokawa et al. discussed the thermodynamic stability of perovskite cathode materials in terms of the stabilization energies and the valence stabilities [40, 41]. Navrotsky et al determined the enthalpies of formation for the perovskite LaMO_3 (*M* = Cr, Fe, Co, and Ni) at room temperature using high-temperature oxide melt solution calorimetry [42].They, subsequently, concluded that the relative thermodynamic stability of the perovskite LaMnO$_3$ decreases in the order of Cr, Fe, Co, Ni. Tanasescu et al correlated the thermodynamic properties with the compositional variables of perovskite ABO_3 (*A* = La, Sr; *B* = Mn, Fe, Co) based on the experiments towards coulometric titration coupled with EMF measurements [43-47]. The relative partial molar free energies, enthalpies, and entropies of oxygen dissolution represented the thermodynamical properties in the perovskite phase. Excellent reviews on lanthanum manganite-based cathodes, other manganite cathodes, lanthanum cobaltite and ferrite cathodes, ferro-cobaltite cathodes, nickelate cathodes are published in near recent past [46, 48].

It is worth mentioning here that the conventional SOFC cathode, strontium-doped lanthanum manganite (LSM), is unsuitable for IT-SOFCs operating below 800 °C. Jiang reviewed and updated the development, understanding, and achievements of the LSM-based cathodes for SOFCs[49]. Their structure, nonstoichiometric, defect model, and, in particular, the relation between the microstructure, their properties (electrical, thermal, mechanical, chemical, and interfacial), and electrochemical performance as well as long-term stability are critically reviewed. The poor electrochemical activity of LSM cathode is chiefly due to its negligible ionic conductivity; therefore, the electrochemical reaction is strictly limited to the TPB [50, 51]. In this regards $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) perovskite oxides are identified as one of the potential IT-SOFC cathode materials. Zhou et al reviewed the current research activities on BSCF-based cathodes for IT-SOFCs [52]. They emphasized on the understanding and optimization of BSCF-based materials. The issues raised by the BSCF cathode are also discussed and analyzed to provide some guidelines in the search for the new generation of cathode materials for IT-SOFCs. Thus, now-a-day studies on development of a number of oxides materials for SOFC cathode applications are directed for improved performance at relatively lower temperatures and high resistance to degradation during operation [30]. An important class of candidate materials for the next generation SOFC cathodes belong to the perovskite related Ruddlesden-Popper (RP) series of layered oxides (formula $A_{n+1}B_nO_{3n+1}$). They exhibit good electrochemical, catalytic and electrical properties as well as thermal and mechanical stability. Chroneos et al published a comprehensive review article on RP series of layered oxides as cathode materials [30].A literature survey pertinent to the cathode materials having K_2NiF_4-type structure, first members of the RP series (for *n* = 1, A_2BO_4) and most relevant to the materials under present study, is given in next subsection.

As discussed above up till now, most of the studies concerned with cathode materials for SOFCare devoted to perovskite type oxides. In near recent past, however, a new family of oxides with

general formulation A_2MO_{4+y} are investigated. The structure of K_2NiF_4-type exhibits some oxygen over-stoichiometry. Preliminary results are promising in terms of oxygen diffusion and surface exchange coefficients.

K_2NiF_4-type Structure Cathode Materials

Ln_2NiO_4-based compounds exhibiting a K_2NiF_4-type structure are normally described as $A_2BO_{4+\delta}$. According to the literature, there are four T, T', T^* and O, possible structures. Amongst them, three tetragonal modifications differ in the transition metal coordination environment, i.e. from 4-fold to 6-fold. Many of the layered cuprates compositions are previously investigated, in general, with respect to their electrical properties and, in particular, superconductivity at low temperatures. K_2NiF_4-type structure consists of the stacking of perovskite ABO_3 layers alternating with rock salt AO layers along the c-direction as shown schematically in Figs. 2 (a) and (b) [53]. Such oxides are of great interest as an oxygen electrode material for applications in various electrochemical solid-state devices. $A_2BO_{4\pm\delta}$ (B = Co, Ni and Cu) compounds exhibit high electronic conductivity. Also, possibility of forming solid solutions with mixed valence of the B-site provides good scope to tailor the physic-chemical properties. In addition, a high concentration of oxygen interstitials offers rapid oxygen transport through crystal, eventually a scope for developing a new type of MIEC cathode materials.

Particularly, the La_2MO_4 is considered for oxygen sensors, oxygen separation membranes and as cathodes for IT-SOFC [16, 54-65]. Therefore, in the subsequent discussions, several performance determining factors of Ln_2MO_4 cathode materials are addressed. Particularly the chemical and thermal stability, the compatibility with traditional electrolytes, the electrical conductivity and the oxygen transport behavior, and the electrochemical properties.
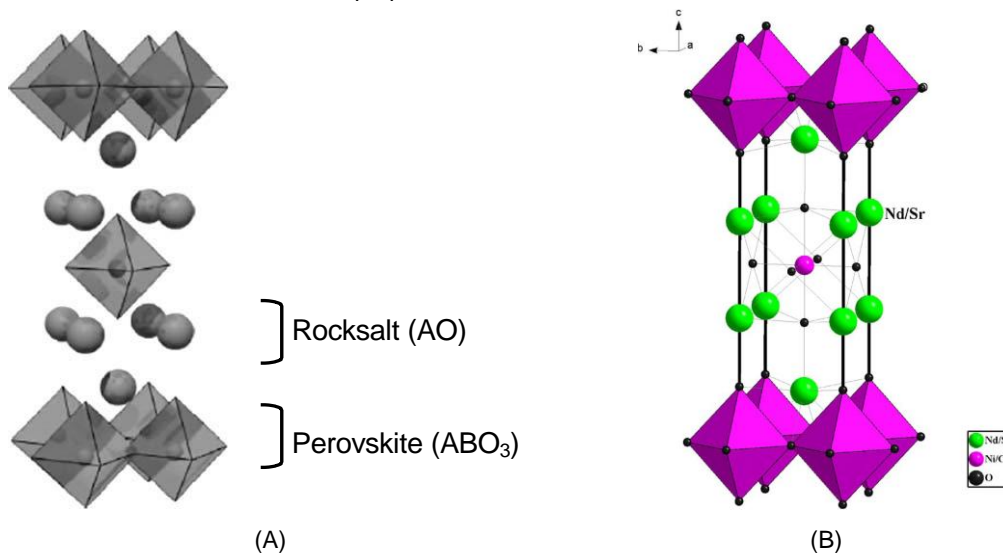

(A)   (B)

Fig.2: (a) and (b) K_2NiF_4 type structure showing alternating AO and ABO₃ layers [16, 53].

References

1.   Fuel Cell Handbook (2002) EG& G technical services, 6[th]Edn. Science Applications International Corporation, Morgantown, West Virginia

2.   N. Q. Minh, T Takahashi (1995) Science and technology of ceramic fuel cells. Elsevier, Amsterdam

3.   O. Yamamoto, *Electrochim. Acta* 45 (2000) 2423

4.   S. C. Singhal, *Mater. Res. Soc. Bull.* 25 (2000) 16

5.   S. Park, J. M. Vohs, R. J. Gorte, *Nature* 404 (2000) 265

6.   S. C. Singhal, *Solid State Ionics* 152–153 (2002) 405

7.   K. Eguchi, H. Kojo, T. Takeguchi, R. Kikuchi, K. Sasaki, *Solid State Ionics* 152–153 (2002) 411

8.   F. Alcaide, P. L. Cabot, E. Brillas, *J. Power Sources* 153 (2006)

9.   M. Belmonte, *Adv. Eng. Mater.* 8 (2006) 693

10.   R. von Helmolt, U. Eberle, *J. Power Sources* 165 (2007) 833

11.   M. Yano, A. Tomita, M. Sano, T. Hibino, *Solid State Ionics* 177 (2007) 3351

12.   A. Bauen and J. Hart, *J. Power Sources* 86 (2000) 482

13.   M. Phongaksorn, A. Yan, M. Ismail, A. Ideris,E.Croiset, S. Corbin, Y. Yoo,219th ECS Meeting, *The Electrochemical Society* (2011)

14.   F. Mauvy, J.-M. Bassat, E. Boehm, J.-P. Manaud, P. Dordor, J.-C. Grenier, *Solid State Ionics* 17– 28 (2003) 158

15.   C. Sun, R. Hui, J. Roller, *J Solid State Electrochem* 1125–1144 (2010) 14

16.   Synthesis and characterization of oxygen permeable composites from Solid Oxide FuelnCell (SOFC) point of view, Ph.D. Thesis byA. P. Khandale, R. T. M. Nagpur University, Nagpur (2010)

17.   C.S. Tedmon, H.S. Spacil, S.P. Mitoff, *J. Electrochem. Soc.* 116 (1969) 1170

18.   B. C. H. Steele,*Solid State Ionics*134(2000) 3-20

19.   V.Dusastre, J. A.Kilner, *Solid State Ionics*126(1999) 163-174

20.   F. S. Galasso, Perovskites and High Tc Superconductors, Gordon & Brach, New York, 1990

21.   H. A. Borges, M. A. Continentino, *Solid State Commun.* 80 (1991) 197

22.   T. D. McColm, J. T. S. Irvine, *Ionics* 7 (2001) 116

23.   V. V. Kharton, F. M. B. Marques, A. Atkinson, *Solid State Ionics* 174 (2004) 135

24.   K. Larbaoui, A. Tadjer, B. Abbar, H. Aourag, B. Khelifa, C. Mathieu, *J. Alloys Compd.* 403 (2005) 1

25.   F. Tietz, H. P. Buchkremer, D. Stover, *J. Electroceram.* 17 (2006) 701

26.   R. V. Vovk, M. A. Obolenskii, A. A. Zavgorodniy, A. V. Bondarenko, I. L. Goulatis, A. V. Samoilov, A. Chroneos, *J. Alloys Compd* .453 (2008) 69

27.   S. J. Skinner*, Int. J. Inorg. Mater.* 3 (2001) 113

28.   B. A. Boukamp, *Nat. Mater.* 2 (2003) 294

29.   S. W. Tao, J. T. S. Irvine, *Nat. Mater.* 2 (2003) 320

30.   A. Chroneos, R. V. Vovk, I. L. Goulatis., L. I. Goulatis, *J. Alloys Compd.*doi: 10.1016/ j.jallcom. 2010.01.071

31.   R. D. Shannon, *Acta Cryst.* A 32 (1976) 751

32.   K. Nomura, S. Tanase, *Solid State Ionics* 98 (1997) 229

33.   A. J. McEvoy, *Solid State Io*nics 135 (2000) 331

34.   S. B. Alder, *Chem. Rev.* 104 (2004) 4791

35.   R. J. A. M. Van, E. H. P. Cordfunke*, J. Solid State Chem*. 93 (1991) 212

36.   J. Mizusaki, *Solid State Ionics* 52 (1992) 79

37.   N. E. Trofimenko, H. Ullmann, *J. Eur. Ceram. Soc.* 20 (2000) 1241

38.   H. Ullmann, N. Trofimenko, *Solid State Ionics* 119 (1999) 1

39.   H. Ullmann, N. Trofimenko, F. Tietz, D. Stover, A. Ahmad-Khanlou, *Solid State Ionics* 138 (2000) 79

40.   H. Yokokawa, N. Sakai, T. Kawada, M. Dokiya, *Solid State Ionics* 52 (1992) 43

41.   H. Yokokawa, T. Kawada, M. Dokiya, *J. Am. Ceram. Soc.* 72 (1989) 152

42.   J. Cheng, A. Navrotsky, *J. Mater. Res.* 20 (2005) 191

43.   C. Sun, R. Hui, J. Roller, *J. Solid State Electrochem.*14 (2010) 1125- 1144

44.   S. Tanasescu, N. D. Totir, D. Neiner, *J. Optoelectronics Adv. Mater*. 3 (2001) 101

45.   S. Tanasescu, N. D. Totir, D.I. Marchidan, *Electrochim. Acta* 43 (1998) 1675

46.   S. Tanasescu, N. D. Totir, D.I. Marchidan, *Solid State Ionics* 119 (1999) 311

47. V. E. Tsipis, V. V. Kharton, *J. Solid State Electrochem.* 12 (2008) 1367

48. S. Chunwen, H. Rob and R. Justin, *J. Solid State Electrochem.* 14(7) (2010) 1125

49. S. P. Jiang, *J. Mater. Sci.* 43 (2008) 6799

50. E. P. Murray, T. Tsai, S. A. Barnett, *Solid State Ionics* 110 (1998) 235

51. E. P. Murray, S. A. Barnett, *Solid State Ionics* 143 (2001) 265

52. W. Zhou, R. Ran, Z. Shao, *J. Power Sources* 192 (2009) 231

53. E. N. Naumovich, M. V. Patrakeev, V. V. Kharton, A. A. Yaremechenko, D. I. Logvinovich, F. M. B. Marques, *Solid State Sci.* 7 (2005) 1353

54. C. N. Munnings, S. J. Skinner, G. Amow, P. S. Whitfiels, I. J. Davidson, *Solid State Ionics* 176 (2005) 1895

55. V. V. Vashook, N. E. Trofimenko, H. Ullmann, L. V. Makhnach, *Solid State Ionics* 131 (2000) 329

56. S. J. Skinner, J. A. Kilner, *Solid State Ionics* 135 (2000) 709

57. L. Minervini, R.W. Grimes, J.A. Kilner, K.E. Sickafus, *J. Mater. Chem.* 10 (2000) 2349

58. F. Mauvy, J. M. Bassat, E. Boehm, J. P. Manaud, P. Dordor, J. C. Grenier, *Solid State Ionics* 158 (2003) 17

59. S. J. Skinner, *Solid State Sci.* 5 (2003) 419

60. J. M. Bassat, P. Odierb, A. Villesuzannea, C. Marinc, M. Pouchard, *Solid State Ionics* 167 (2004) 341

61. H. Zhao, F. Mauvy, C. Lalanne, J.M. Bassat, S. Fourcade, J.C. Grenier, M. Pouchard, *Solid State Ionics* 179 (2004) 2000

62. C. Frayret, A. Villesuzanne, M. Pouchard, *Chem. Mater.* 17 (2005) 6538

63. M. Schroeder, M. A. Dragan, *J. Mater. Sci.* 42 (2007) 1972

64. A. R. Cleave, J. A. Kilner, S. J. Skinner, S. T. Murphy, R. W. Grimes, *Solid State Ionics* 179 (2008) 823

65. M. Yashima, M. Enoki, T. Wakita, R. Ali, Y. Matsushita, F. Izumi, T. Ishihara, *J. Am. Chem. Soc.* 130 (2008) 2762.

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