

Perovskite materials for SOFC cathodes.



Leopoldo Suescun



URUGUAY

Laboratorio de Cristalografía, Estado Sólido y Materiales (Cryssmat-Lab). Facultad de Química, Universidad de la República Montevideo, Uruguay



Association

II Polish Forum on Fuel Cells and Hydrogen Technologies 7-10 IX 2009, Kocierz



Overview

- Introduction
- Structural requirements of perovskite SOFC cathodes
- LSMs work at high temperatures
- Structural flexibility of LSCFs
- Oxygen vacancy stabilization in BSCFs and BSZF
- Perovskites with other transition metals
- 2D vs 3D ionic conductors
- Where should we be looking? There's plenty of room...

Introduction

- ➤ Function of the cathode of a SOFC: provide the O²⁻ anions that oxidate the the fuel at the anode's surface. cathode: 1/2O₂(g) + 2e- → O²⁻(s) anode: H₂(g) + O²⁻(s) → H₂O(g) + 2e-
- Electrochemical limiting step at the cathode:
 Oxygen reduction in the cathode's surface.
- Multiple mechanisms for oxygen incorporation at the cathode, all requiring electronic conductivity, some additional ionic conductivity.
- Purely electronic conductors vs. Mixed electronic-ionic coductors for cathode materials: activity only at Triple Phase Boundaries vs. Active surface equals surface exposed to O₂.



Adler SB, Chem. Rev. 2004, 104, 4791-4843



Introduction

- Operation temperature has to equilibrate these factors:
 - Oxygen reduction is a thermally activated process, cell operation at high temperatures increases oxygen incorporation rates independently of the mechanism.
 - Chemical and mechanical stability degrade with higher ion mobility and larger expansion-contraction cycles, cell operation at low temperatures increases durability independently of the materials used.
- These two opposing factors drive current research: Find the cathode-electrolyte-anode combination that operates with the highest efficiency at the lowest possible temperatures.
 - Search for novel cathode, electrolyte and anode materials and processing conditions.



Adler SB, Chem. Rev. 2004, 104, 4791-4843 Dąbrowski B. (2005) Personal Commnication

Structural requirements

Perovskite Structure:

- > 3D network of corner-connected BX_6 octahedra.
- \blacktriangleright B is a small cation (e.g. Mn⁴⁺) in the center of the octahedra.
- A is a large cation (e.g. Sr²⁺) occupying the cubo-octahedral holes generated by O atoms.
- Goldschmidt tolerance factor t describes the geometrical relation between A-X and B-X bond distances imposed by the model.
- A perfect cubic perovskite corresponds to *t*=1. When A is smaller or B larger than expected (within certain range ~0.8<t<1) distorted perovskite structures are found with lower than cubic symmetry.</p>
- > Disordered oxygen vacancies preserve high symmetry, ordering produces distortion.

 $t = \frac{\langle A - X \rangle}{\sqrt{2} \langle B - X \rangle} \approx 1$

Structural requirements: e- conductivity

- Electronic conductivity requires heterovalent atoms at the B-site showing more than one stable oxidation state compatible with the octahedral geometry.
 M = Mn^{3+/4+}, Fe^{3+/4+}, Co^{2+/3+/4+}, Ni^{2+/3+}.
- Overlap between M3d and O2p electronic orbitals provides a path for electron hoping between neighbouring M cations and explains the existence of electronic conductivity (and magnetic properties) in perovskites.
- M-O bond distance and the M-O-M angle (θ) determine the degree of overlap of successive M3d orbitals with the same O2p orbital, or the degree of orbital overlap of each M3d-O2p-M3d triplet. The higher the bond order (individual M3d-O2p overlap extent) and the larger the M-O-M angle the wider the conduction band and the largest conductivity.



Bandwidth **w** α **k*cos²(θ)**

Structural requirements: ionic conductivity

- High concentration of mobile oxygen ion vacancies.
- Equal energy of different oxygen sites.
- Physical path of migration has to impose a low energetic barrier smaller than
 - thermal excitation energy of the ions
 - electric potential energy among the occupied and vacant sites.
- Weak M-O bonding energies.
- In conventional 3D perovskite systems these conditions are fulfilled when:
 - heterovalent atoms exist in the B site (3d transition metals) that allow a change in coordination number and charge without significant network distortion.
 - the network is isotropic (cubic or slightly distorted pseudo-cubic) with many vacancies.

Moguensen M. et al (2004) Solid State Ionics 174, 279

Structural requirements: overview





MOST FREQUENT STRUCTURAL DISTORTIONS IN PEROVSKITES STRONGLY AFFECT PARAMETERS REQUIRED FOR HIGH ELECTRONIC AND IONIC CONDUCTIVITY.

> Cation size mismatch produces octahedral tilting thus M-O-M angle reduction and inequivalent oxygen atoms.

> Jahn-Teller or electronic-originated effects affect M-O distances, produce charge localization and may produce tilting.



Second Polish Forum

ring

Overview

- Introduction
- Structural requirements of perovskite SOFC cathodes
- > Why do LSMs work
- Structural flexibility of LSCFs
- Oxygen vacancy stabilization in BSCFs and BSZF
- Perovskites with other transition metals
- 2D vs 3D ionic conductors
- Where should we be looking? There's plenty of room...

Why do LSMs work

- LSMs (La_{1-x}Sr_xMnO_{3-δ}) with 0.2<x<0.4 was described by Goodenough as a good electronic conductor with cubic or slightly distorted rhombohedral structure showing a few oxygen vacancies in equilibrium at low temperatures.
- > Advantages:
 - Simple preparation
 - Exceptional chemical stability at operation temperature (~1150 K)
 - Very low reactivity with YSZ.
 - Smooth $R \rightarrow C$ phase transition with a very small TEC variation.
- > Drawbacks:
 - Structurally rigid.
 - Low surface electrochemical activity.
 - Low number of oxygen vacancies even at high temperatures.



Second Polish Forum

 Goodenough J.B. Phys Rev (1955) 100, 564.

 Chmaissem O. et al, (2003) PRB 67, 094431
 10

 Adapted from Corbel, G. et al, (2005) Sol. State Sci. 7, 1216.

Why do LSMs work

- Manganites are structurally rigid:
 - Strong correlation between Mn charge and oxygen vacancies due to rigid Mnⁿ⁺ coordination preferences.
- ➤ Vacancy ordered compounds in the La_{1-x}Sr_xMnO_{3-δ} system octal with 0.5< δ <0.125 confirm that only certain polyhedra are compatible with certain oxidation states:</p> $Mn^{3+} d^{4}$
 - ➢ Mn⁴⁺ OCTAHEDRON
 - ➢ Mn³⁺ OCTAHEDRON, SQUARE-BASED PYRAMID
 - ➢ Mn²⁺ OCTAHEDRON, TETRAHEDRON



Suescun L. et al (2007), JSSC 180, 1698. Dąbrowski B. et al (2006), personal communication Casey PS. et al (2006), JSSC 179, 1375.

Second Polish Forum







JT or pyramid

octahedron



Why do LSMs work

- Excellent match with electrolyte allow for operation at high temperatures that compensate for unfavorable properties:
 - Oxygen vacancies form at high temperature due to the shift of Mn⁴⁺/Mn³⁺ equilibrium concentration towards Mn³⁺.
 - Formation of disordered vacancies favor cubic structure increasing both electronic and ionic conductivity.
- LSMs seem to work mainly due to high temperature of operation!.

- La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} materials were proposed as cathodes for SOFCs after Teraoka et al showed their excellent ionic and electronic conductivity at low temperatures (600 - 800 °C).
- > Advantages:
 - Simple preparation.
 - Significant number of oxygen vacancies at all temperatures for Sr-rich compounds.
 - Fast oxygen exchange at the surface due to high activity of Co and Fe cations does not require as high operation temperature as manganites.
 - Keep cubic or pseudo-cubic structures over a wide range of x, y.
- Disadvantages:
 - Very reactive against traditional electrolyte YSZ.
 - High and variable TEC due to Co/Fe spin state changes.
 - Marked changes in equilibrium oxygen content with T.

Teraoka Y. et al, (1985) Chem. Lett. 1743. Šwierczek K. et al, (2009) JSSC 182, 280.





- LSCFs require low preparation temperatures (as low as 800 °C) therefore it's possible to make nanostructured cathodes.
 45° rotated
- Reduced electrochemical activity at low temperatures is compensated by large surface area for oxygen reduction achieving high performance cathodes.
- Considering the small distortions from symmetry in LSCFs reported to date, all nanosized LSCFs are cubic.
- Crystal growth during operation should be considered if a correct assessment of performance decay is to be made.



► By low temperature synthesis nanostructured $La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathodes over $Ce_{0.9}Gd_{0.1}O_{1.95}$ show very promising electrochemical performances at low T.



Baqué L et al, Electrochem. Comm. 10 (2008) 1905.

Second Polish Forum

- LSCFs show three serious drawbacks:
 - Reactivity of Cobalt perovskites limit maximum processing and operation temperatures and electrolyte composition.
 - Thermal expansion of cobaltites at ~700 °C is large compared with common electrolytes.
 - Spin state, phase and vacancy ordering transitions commonly observed in cobaltites and ferrites produce jumps in TEC.



- Very flexible Fe and Co cations help fulfill the desired characteristics for maximum electronic and ionic conductivity.
 - Several available oxidation states (Fe^{3+/4+}, Co^{2+/3+/4+}).
 - Several stable polyhedra (octahedra, pyramid, tetraedra) with variable size (depending on low/intemediate/high spin state).
 - Minimum correlation among charge and oxygen vacancies.
- \succ Example: SrCo_{1-y}Fe_yO_{3- δ}.
 - Over the whole y range oxygen vacancy ordered phases exist but few have been recongnized.
 - Although vacancy ordered, phases are still good conductors.
 - \blacktriangleright Fe³⁺/Co³⁺ found in octahedral, pyramidal and tetrahedral coordination.
 - > Difficulty to achieve Co⁴⁺ at normal p_{O_2} keeps number of vacancies high.
- LSCFs have pushed the search for better electrolyte materials compatible with Co-rich cathodes.



Šwierczek K. et al, (2009) J. Solid State Chem. 182, 280. Hodges JP et al, (2000) J. Solid State Chem. 151, 190. Dąbrowski B. et al, (2007) personal communication.

Oxygen vacancy stabilization in BSCFs

- Novel Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_xO_y (x≈0.2) cathodes combine the cubic structure of LSCFs with the presence of a significant amount of oxygen vacancies virtually constant from RT to 700 °C.
- Oxygen vacancy and cubic symmetry stabilization are achieved by:
 - Absence of Ln³⁺ in the A site which pushes average
 B-site charge up.
 - High oxidation potential of the Co³⁺/Co⁴⁺ pair that keeps oxygen content low at normal oxygen pressures.
 - A-site disorder of large Ba²⁺ and and medium size Sr²⁺ cations that prevent oxygen vacancy ordering.

CGIDS Zongping Shao & Sossina M. Haile Materials Science, California Institute of Technology, Pasadena, California 91125, USA Fuel cells directly and efficiently convert chemical energy to electrical energy ¹ . Of the various fuel cell types, solid-oxide fuel cells (SOFCs) combine the benefits of environmentally benign power generation with fuel flexibility. However, the necessity for high operating temperatures (800–1,000 °C) has resulted in high a costs and materials compatibility challenges ² . As a consequence, significant effort has been devoted to the development of inter- mediate-temperature (500–700 °C) SOFCs. A key obstacle to reduced-temperature operation of SOFCs is the poor activity of (traditional cathode materials for electrochemical reduced tem- temperature SOFC operation. BSCF, incorporated into the thin-film doped ceria fuel cell, exhibits high power densities (1,010 mW cm ⁻² and 402 mW cm ⁻² at 600 °C and 500 °C, respect- ively) when operated with humidified hydrogen as the fuel and air as the cathode gas. We further demostrate that BSCF is the ideally suited to 'single-chamber' fuel-cell operation, where anode and cathode reactions take place within the same physical chamber ³ . The high power output of BSCF cathodes results from the high rate of oxygen diffusion through the material. By enabling operation at reduced temperatures, BSCF cathodes	A high-performance cathode for the next generation of solid-oxide fuel	res res ren at ~(of
Zongping Shao & Sossina M. Haile Materials Science, California Institute of Technology, Pasadena, California 91125, USA Fuel cells directly and efficiently convert chemical energy to electrical energy ¹ . Of the various fuel cell types, solid-oxide fuel cells (SOFCs) combine the benefits of environmentally benign power generation with fuel flexibility. However, the necessity for high operating temperatures (800–1,000 °C) has resulted in high costs and materials compatibility challenges ² . As a consequence, significant effort has been devoted to the development of inter- mediate-temperature (500–700 °C) SOFCs. A key obstacle to reduced-temperature operation of SOFCs is the poor activity of traditional cathode materials for electrochemical reduction of $Co_{0.8}Fe_{0.2}O_{3-6}(BSCF)$ as a new cathode material for reduced temperature SOFC operation. BSCF, incorporated into thin-film doped ceria fuel cell, exhibits high power densities (1,010 mW cm ⁻² and 402 mW cm ⁻² at 600 °C and 500 °C, respect- air as the cathode gas. We further demonstrate that BSCF is tideally suited to 'single-chamber' fuel-cell operation, where anode and cathode reactions take place within the same physical chamber ³ . The high power output of BSCF cathodes results from the high rate of oxygen diffusion through the material. By enabling operation at reduced temperatures, BSCF cathodes	CCIIS	de
Materials Science, California Institute of Technology, Pasadena, California 91125, USA Fuel cells directly and efficiently convert chemical energy to electrical energy ¹ . Of the various fuel cell types, solid-oxide fuel cells (SOFCs) combine the benefits of environmentally benign power generation with fuel flexibility. However, the necessity for high operating temperatures (800–1,000 °C) has resulted in high costs and materials compatibility challenges ² . As a consequence, significant effort has been devoted to the development of inter- mediate-temperature (500–700 °C) SOFCs. A key obstacle to reduced-temperature operation of SOFCs is the poor activity of traditional cathode materials for electrochemical reduction of boxygen in this temperature regime ⁴ . Here we present Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O ₃₋₆ (BSCF) as a new cathode material for reduced temperature SOFC operation. BSCF, incorporated into thin-film doped ceria fuel cell, exhibits high power densities (1,010 mW cm ⁻² and 402 mW cm ⁻² at 600 °C and 500 °C, respect- air as the cathode gas. We further demonstrate that BSCF is tideally suited to 'single-chamber' fuel-cell operation, where anode and cathode reactions take place within the same physical chamber ³ . The high power output of BSCF cathodes results from the high rate of oxygen diffusion through the material. By enabling operation at reduced temperatures, BSCF cathodes com-	Zongping Shao & Sossina M. Haile	sei
Fuel cells directly and efficiently convert chemical energy to electrical energy ¹ . Of the various fuel cell types, solid-oxide fuel cells (SOFCs) combine the benefits of environmentally benign power generation with fuel flexibility. However, the necessity for high operating temperatures (800–1,000 °C) has resulted in high costs and materials compatibility challenges ² . As a consequence, significant effort has been devoted to the development of inter- mediate-temperature (500–700 °C) SOFCs. A key obstacle to reduced-temperature operation of SOFCs is the poor activity of traditional cathode materials for electrochemical reduction of oxygen in this temperature regime ² . Here we present Ba _{0.5} Sr _{0.5} $Co_{0.8}Fe_{0.2}O_{3-\delta}(BSCF)$ as a new cathode material for reduced temperature SOFC operation. BSCF, incorporated into a thin-film doped ceria fuel cell, exhibits high power densities (1,010 mW cm ⁻² and 402 mW cm ⁻² at 600 °C and 500 °C, respect- air as the cathode gas. We further demonstrate that BSCF is tideally suited to 'single-chamber' fuel-cell operation, where anode and cathode reactions take place within the same physical chamber ³ . The high power output of BSCF cathodes results from the high rate of oxygen diffusion through the material. By enabling operation at reduced temperatures, BSCF cathodes com-	Materials Science, California Institute of Technology, Pasadena, California 91125, USA	pe pa
may result in writespread practical implementation of SOFCs.	Fuel cells directly and efficiently convert chemical energy to electrical energy ¹ . Of the various fuel cell types, solid-oxide fuel cells (SOFCs) combine the benefits of environmentally benign power generation with fuel flexibility. However, the necessity for high operating temperatures ($800-1,000$ °C) has resulted in high costs and materials compatibility challenges ² . As a consequence, significant effort has been devoted to the development of intermediate-temperature ($500-700$ °C) SOFCs. A key obstacle to reduced-temperature operation of SOFCs is the poor activity of traditional cathode materials for electrochemical reduction of oxygen in this temperature regime ⁴ . Here we present Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-$\delta}$(BSCF) as a new cathode material for reduced temperature SOFC operation. BSCE, incorporated into a thin-film doped ceria fuel cell, exhibits high power densities (1,010 mW cm⁻² and 402 mW cm⁻² at 600 °C and 500 °C, respectively) when operated with humidified hydrogen as the fuel and air as the cathode gas. We further demonstrate that BSCF is ideally suited to 'single-chamber' fuel-cell operation, where anode and cathode reactions take place within the same physical chamber³. The high power output of BSCF cathodes results from the high rate of oxygen diffusion through the material. By enabling operation at reduced temperatures, BSCF cathodes may result in widespread practical implementation of SOFCs.}	ch ele µr lay ad wa to an (F lah (S th va pc ab an th wc ac th co th co co th va co co co co co co co co co co

oxygen in this temperature regime². Here we present $Ba_{0.5}Sr_{0.5}$ -Co_{0.8}Fe_{0.2}O_{3- δ}(BSCF) as a new cathode material for reducedtemperature SOFC operation. BSCF, incorporated into a

Shao ZP, Haile SM, Nature (2004) 431, 170

Oxygen vacancy stabilization in BSCFs

The resulting material overperforms LSCFs due to higher oxygen conductivity caused by higher vacancy concentration.

ntensity /Counts

- Main Drawbacks:
 - Very poor stability of the perovskite structure upon decomposition into hexagonal Co compounds below formation temperature (950°C).
 - The high reactivity with atmospheric carbon dioxide to form Ba_{1-x}Sr_xCO₃.
 - Ba is expensive and environmentally not friendly...

Arnold M. et al Chem. Mater. (2008) 20, 5851. Yan A.Y. et al Appl. Catalysis B (2007) 76, 320.



Cobalt-free cathode BSZFs

- > $Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-\delta}$ has just been proposed by Feldhoff to replace BSCFs.
- This Co-free perovskite is more stable than BSCFs at low and intermediate temperatures and shows equivalent ionic and electronic conductivity with significant and stable number of oxygen vacancies in a cubic structure.
- Additionally it shows a small thermal expansion coefficient below 700 °C.
- Drawback: it has been shown that Fe undergoes a spin state transition that produces a significant step in thermal expansion coefficient around 700 °C.



Feldhoff A. et al J. Solid State Chem. (2009), in press doi:10.1016/j.jssc.2009.07.058

Perovskites with other transiton metals

- ► $Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-\delta}$, Nickelates (LnFe_{1-x}Ni_xO_{3-\delta}), Cuprates (LaBaCu(Co,Fe)O_{3-\delta}), etc, have been recently proposed as SOFC cathodes.
- Most of them base their usefulness in either the relative high electrochemical activity of different transition metals oxidation/reduction couples or in the stabilization of vacancies.
- \blacktriangleright Ni²⁺/Ni³⁺ and Cu²⁺/Cu³⁺ pairs provides a low energy path for oxygen activation.
- Zn²⁺ in BSZF plays two important roles replacing Co in BSCF:
 - ▶ It shifts the electronic charge to Fe that, at normal oxygen pressures, remains in a mix 3+/4+ state.
 - It's lower coodination number shifts oxygen towards Fe increasing its coordination number without removing vacancies
 - It provides disordered vacant sites around its tetrahedral but flexible coordination environment that could be used for hoping.

Feldhoff A. et al (2009) JSSC, in press doi:10.1016/j.jssc.2009.07.058 Zając W. et al (2007) J. Power Sources, 173, 675. Zhou QJ. et al (2009) Electrochem. Commun. 11 80.

Variables for the design



2D vs 3D ionic conductors

- Other perovskite-type structures have been proposed and tested as SOFC cathodes. Among them two types of very promising layered materials are currently being tested:
 - 214 or R-P n=1 type La₂NiO_{4+δ} (A₂BO₄): Layered Rudlesden-Popper perovskite with intersticial oxygen in LaO layer.
 Very high oxygen icorporation rates.
 Ionic conductivity through hoping of intersticial oxygen excess.
 (Skinner S.J., Kilner J.A., Solid State Ionics (2000) 135, 709)
 - 112 or layered double perovskites LnBaCo₂O_{5.5±δ} (AA'B₂O_{6-δ}) Layered perovskite with oxygen vacancies in LnO0.5±d layer. Also high electrochemical activity at cathode's surface Ionic conductivity through vacancy hoping like in 3D perovskites.

(Kim G. et al, Appl. Phys. Lett. (2006) 88, 24103)



Where should we be looking...

- Additionally to many alternative compositions within the simple or complex perovskite types these options still remain:
 - Microstructure patterning
 - Composite formation
 - Activation coatings
 - ≻ ..
- Economical viability...
- Environmental friendlyness ...

Yoon J et al (2007), Appl. Surface Science 254, 266. Princivalle & Djurado (2008), Solid State Ionics 179, 1921 Tian R et al (2008), J. Pow. Sources 185, 1247.



Keywords: Low-temperature solid oxide fuel cells trodes to significantly increase the electrode activity of both cathodes and anodes. A peak power density of 0.46 W cm⁻² and area specific interfacial polarization resistance of 0.36 Ω cm² are achieved at 600 °C for single cells consisting of Ni-SDC anodes, LSM cathodes, and SDC electrolytes. The cell performances

Second Polish Forum

ate

ivitv

There's plenty of room...



Acknowledgments

J. Molenda, K. Šwierczek, A. Milewska and W. Zając

Department of Solid State Chemistry, Faculty of Materials Science, AGH University of Science and Technology.

Bogdan Dąbrowski

Physics Department, NIU and Materials Science Division at ANL, USA

 A.W. Mombrú, H. Pardo, R. J. Faccio, L. Fernández, C. Goyenola.
 Crystallograpy, Solid State and Materials Lab. (Cryssmat-Lab)/DETEMA, Facultad de Química, Universidad de la República, Montevideo, Uruguay.

Dziękujemy za uwagę państwa rodzaju!

(Are you kidding? How in the world could I say it?)

Questions? Comments?