

## THE FERMI ENERGY IN ACCEPTOR DOPED SrTiO<sub>3</sub> AND BaTiO<sub>3</sub>

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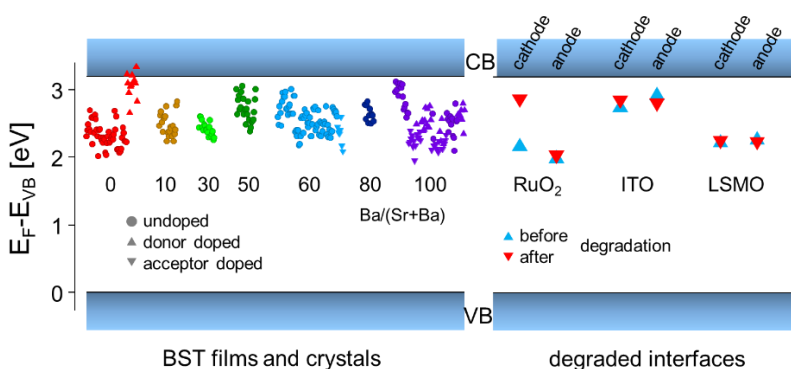
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**Key Words:** SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, acceptor doping, Fermi energy

In order to evaluate the presence of space charge layers and the magnitude of band bending at electrode interfaces of mixed ionic-electronic conductors we have evaluated the Fermi energies in the bulk and at interfaces of acceptor-doped SrTiO<sub>3</sub>, BaTiO<sub>3</sub> and (Ba,Sr)TiO<sub>3</sub>. While the interface Fermi energy can be directly obtained using photoelectron spectroscopy (XPS) if conducting electrode materials are deposited, the determination of the bulk Fermi energy is more challenging due to the high resistivity of the samples. One approach is to use XPS on thin films deposited on conducting samples. In general, we observed a good agreement between upper and lower limits of Fermi energies at thin films surfaces and at interfaces. Surprisingly, the Fermi energy is hardly observed below  $E_F - E_{VB} \approx 2\text{eV}$  (see Fig. 1), although defect chemistry calculations predict values as low as  $E_F - E_{VB} \approx 2\text{eV}$  for acceptor doped samples, such as Fe-doped SrTiO<sub>3</sub> or Mn-doped BaTiO<sub>3</sub>.<sup>c,d</sup> Even at anode interfaces of ionically polarized Fe-doped SrTiO<sub>3</sub> single crystals,<sup>e</sup> at which the oxygen vacancy concentration should be very low, we have not observed lower Fermi energies.



*Figure 1 – (left) Fermi energy at surfaces of differently doped polycrystalline (Ba,Sr)TiO<sub>3</sub> thin films. Each data point represents one sample prepared using different parameters and on different substrates; (right) Fermi level positions at anode and cathode interfaces of Fe-doped SrTiO<sub>3</sub> single crystals before and after ionic polarization at 210°C.*

The too high Fermi energies might result from the presence of additional defect levels, which pin the Fermi energy. In order to resolve the discrepancy, temperature dependent conductivity measurements have been applied. Starting with electronically highly conducting reduced samples, these are slowly re-oxidized during temperature cycling with permanently recording the conductance. These measurements reveal activation energies in dependence on conductivity, which can be directly compared to defect chemistry calculations. In particular, the activation energy should exhibit a plateau in dependence on conductivity if the Fermi level is pinned at a certain defect level. This approach allows to quantify the energy levels of defects in the relevant temperature regime, in particular those related the 3+/2+ valence change of Fe and Mn. Such levels are clearly observed for single crystal and polycrystalline BaTiO<sub>3</sub> but not for Fe-doped SrTiO<sub>3</sub>. In the latter case, the samples directly convert from metallic behavior at resistivities  $<10^6\text{ S/cm}$  to p-type behavior. All measurements being in good agreement with present defect chemistry models. The origin of the too high Fermi energy therefore remains unresolved.

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## SELF-ASSEMBLED GRAPHENE DERIVATIVES USED AS HTLs FOR HIGHLY EFFICIENT INVERTED PEROVSKITE SOLAR CELLS

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**Key Words:** perovskite solar cells; graphene derivatives; layer by layer; hole transporting layers; charge-extraction.

The performance of inverted perovskite solar cells (PSCs) based on graphene oxide hole transporting materials is still unsatisfactory due to the high degree of surface oxygen contents and the insulating property. In this study, thickness-controlled and full-coverage graphene oxide films prepared by layer-by-layer self-assembly technique are firstly developed as hole transporting layers (HTLs) in PSCs. Meanwhile, conductivity tunable reduced graphene oxide films are *in-situ* prepared by an environment-friendly and efficient reductant system. A superior PCE of 16.28% based on rGO as prepared is obtained, resulting in an increment by approximately 33% compared with 12.26% of the device based on GO-1 as mentioned. At the same time, this work reveals an anomalous charge-extraction behavior of PSCs based on GO or rGO HTLs. Competition effect of interfacial recombination, charge transportation and radiation recombination in this process are proposed to analyze the internal mechanisms. This work provides a facile and novel method to prepare GO or rGO films, which can be used as efficient charge-extraction layers and even electrodes in inverted PSCs.

**Reference:** Yin, X.; Zhou, Y.; Han, J.; Nan, H.; Tai, M.; Gu, Y.; Li, J.; Lin, H.\*, Highly efficient inverted perovskite solar cells based on self-assembled graphene derivatives. *Journal of Materials Chemistry A*, 2018, 6, 20702-20711.

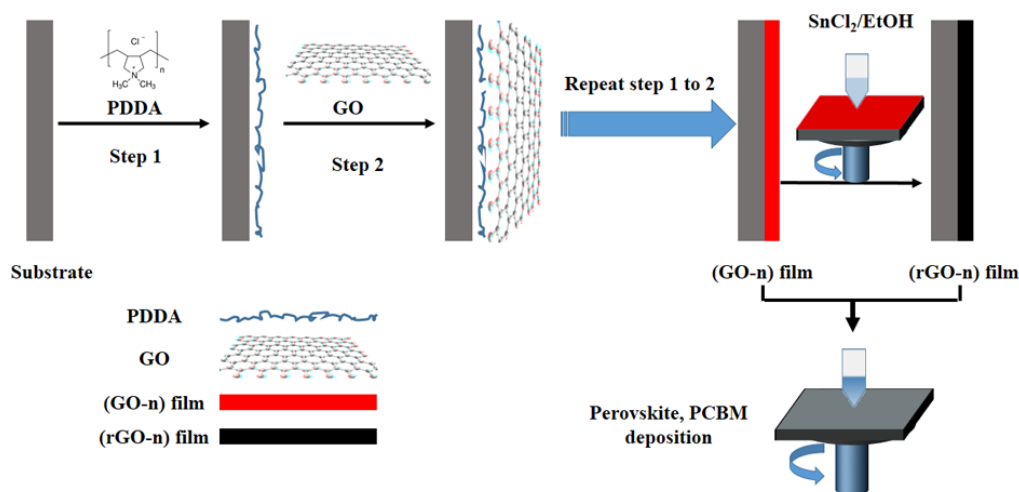


Figure 1 –Procedures to prepare thickness-controlled GO and conductivity tunable rGO films used as HTMs in PSCs.

## **THERMOELECTRIC PROPERTIES OF GRAPHENE INCORPORATED THERMOELECTRIC MATERIALS**

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**Key Words:** Graphene, Thermoelectric, thermal conductivity, electric conductivity, grainboundary scattering

Thermoelectric materials, which can change the waste heat into the usable electricity, are interested in various field of applications such as vehicle, ship, power plane, and so on. To enhance the thermoelectric properties, high electrical conductivity, high Seebeck coefficient, and low thermal conductivity should be conducted, however, the trade-off relation between electronic property and thermal property in terms of carrier concentration could be the bottle-neck on the enhancement of thermoelectric properties of the materials. In this presentation, we discuss with the graphene incorporation in the conventional thermoelectric materials, which could lead to independently control electric and thermal properties.

## PROTON UPTAKE IN THE MIXED IONIC AND ELECTRONIC CONDUCTORS $\text{Ba}_{1-x}\text{Sr}_x\text{FeO}_{3-dx}$

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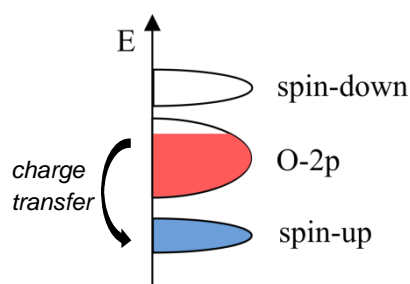
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**Key Words:** protonic ceramic fuel cell, DFT, electronic structure, defect interaction

Cathode materials for proton-conducting ceramic fuel cells (PCFC) should combine electronic conductivity with adequate proton conductivity and thereby extend the water formation process from the triple phase boundary to the entire surface of the porous cathode. A variety of such materials including perovskite-structured  $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_3$  has been studied experimentally with regard to proton uptake, revealing a systematically lower proton concentration than in electrolyte materials and a peculiar interaction between electronic charge carriers (i.e. holes) and ionic charge carriers (i.e. protons). [1]



In this study, the electronic structure of the model material  $\text{BaFeO}_3$  is investigated in  $2 \times 2 \times 2$  supercells by means of DFT+U (PBE functional) and hybrid DFT (HSE06 functional). Special focus is laid on the characteristics of the O2p states since they dominate the valence band in oxides, and are involved in O-H bond formation upon proton uptake (protons are incorporated in the form of hydroxide ions on oxide ion sites).

The calculations show that strong correlation effects of Fe3d electrons lead to a significant energy separation of spin-up and spin-down sub-bands. The spin-up band eventually falls below the O2p states and thus

triggers a negative charge transfer from the oxide ions to the iron ions. These results are in line with an experimental x-ray spectroscopic study on  $\text{BaFeO}_3$  thin films. [2]. The negative charge transfer reduces the absolute charge on the oxide ions and as such the oxide ion's basicity. Since the basicity of the oxide ion plays a decisive role in the hydration thermodynamics of solid oxides, the negative charge transfer could explain why the measured proton uptake [1] is lower than the threshold expected from defect chemical modelling.

The formation of oxygen vacancies is accompanied by a simultaneous annihilation of holes and thereby changes the occupancy of the O2p states. The vacancy formation energy increases with decreasing hole concentration in the system. The hydration enthalpy also depends on hole concentration (varying between zero and  $\approx -1$  eV), although the hydration reaction (dissociative water incorporation into oxygen vacancies) is a pure acid-base reaction. Both effects are discussed in the context of the electronic structure of  $\text{BaFeO}_3$ .

Finally, the implications of the electronic structure on the proton uptake are discussed for related compounds  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$  and  $\text{SrFeO}_3$ , with the latter showing the least favorable proton uptake.

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## CRYSTAL STRUCTURE, OXYGEN NONSTOICHIOMETRY, HYDRATION AND CONDUCTIVITY BaZr<sub>1-x</sub>MxO<sub>3-d</sub> (M=Pr, Nd, Y, Co)

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**Key Words:** perovskite, double perovskite, defect structure, nonstoichiometry.

Partially substituted perovskite-like barium zirconates with general formula BaZr<sub>1-x</sub>MxO<sub>3-d</sub> possess oxygen-ion and proton conductivity and, therefore, may be promising as electrolytes for intermediate temperature solid oxide fuel cells. The aim of this work was to study the crystal structure, thermal and chemical expansion, water uptake, oxygen nonstoichiometry, total conductivity and Seebeck coefficient of zirconates BaZr<sub>1-x</sub>MxO<sub>3-d</sub> (M=Pr, Nd, Y, Co) in the atmospheres with different levels of humidity ( $\log(p_{H_2O}/atm.) = -1.75; -2.5; -3.5$ ) as a function of oxygen partial pressure ( $\log(p_{O_2}/atm.) = -20 - -0.67$ ) and temperature ( $T = 25 - 1050$  °C).

Synthesis of the samples was carried out by glycerol-nitrate method. The phase composition of the as-prepared powders was analyzed by the X-ray diffraction (XRD). Room temperature and high temperature XRD studies were carried out using Shimadzu XRD-7000 diffractometer equipped with high temperature chamber HTK 16N (Anton Paar GmbH). Thermal and chemical expansion was also measured using DIL 402 C dilatometer (Netzsch GmbH). Oxygen nonstoichiometry was studied by solid state coulometric titration and thermogravimetry. Electrical conductivity and Seebeck coefficient were measured simultaneously in the same setup.

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# LOCAL STRUCTURAL ANALYSIS ON HYDRATION BEHAVIOR IN DOPED AZrO<sub>3</sub> (A = Ba, Ca) PROTONIC CONDUCTORS

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**Key Words:** Protonic conductor, perovskite-type oxide, hydration, local structure, solid-state NMR

Perovskite-type protonic conductors are candidate electrolytes for intermediate temperature solid oxide fuel cells. For practical application, further improvement in proton conductivity is needed. Proton migration in these materials has been reported to be limited by trapping effects of protons by acceptor dopants [1]. In addition, it is suggested that the formation of percolation path with the trapped protons can lower the activation barrier for long-range proton migration and result in enhancement of proton conductivity. The formation of this percolation path is dominated by the location of protons and their concentrations, and higher proton concentration than the percolation limit is necessary for long range transport of protons. To increase or control the proton concentration in the material, understanding of hydration behavior is important because protons are incorporated into the material via hydration reaction of water vapor and oxygen vacancies. Therefore, this study focuses on investigation of hydration behavior from the local structural viewpoint with respect to protons and oxygen vacancies to explore a strategy to improve proton conductivity. For this purpose, solid-state nuclear magnetic resonance combined with density functional theory (DFT) calculations is used to elucidate the local structure of protons and oxygen vacancies since this technique is sensitive to the difference in chemical environment of probing nuclei. In the previous study base on <sup>45</sup>Sc NMR analysis, difference in the local structure around oxygen vacancies in Sc-doped AZrO<sub>3</sub> (A = Ba, Ca) is suggested to be related to the hydration behavior [2]. To clarify the influence of the local structure around oxygen vacancies to the hydration behavior, the electric-field gradient (EFG) at Sc sites, an indicator of the local structure, in Sc-doped AZrO<sub>3</sub> is calculated by DFT calculation and compared with <sup>45</sup>Sc NMR results. EFG at Sc sites is derived from the charge of oxide ions surrounding the nucleus. When the symmetry of the surrounding oxide ions is lowered due to the formation of the oxygen vacancy, large gradient in the electric-field at the Sc site is generated. This EFG interacts with the electric quadrupole moment of Sc nucleus, and this interaction can be observed by <sup>45</sup>Sc NMR.

Figure 1 shows the EFG at Sc sites, represented as the quadrupole coupling constant  $C_Q$ , obtained from DFT calculation and <sup>45</sup>Sc NMR results for Sc-doped BaZrO<sub>3</sub> and CaZrO<sub>3</sub>.  $C_Q$  of two different 5-coordinated Sc is calculated in the case of CaZrO<sub>3</sub> because CaZrO<sub>3</sub> has two crystallographically different oxide ion sites. The  $C_Q$  of Sc sites in Ba-Sc oxides is also calculated and shown as a reference. All the reference oxides have 6-coordinated Sc, and their  $C_Q$  shows good agreement with the NMR results. In the case of 5-coordinated Sc in BaZrO<sub>3</sub> and CaZrO<sub>3</sub>,  $C_Q$  from DFT calculation tends to show larger value compared to the NMR results. However, the trend agrees with the NMR results. In the NMR results, BaZrO<sub>3</sub> shows larger  $C_Q$  compared to CaZrO<sub>3</sub> which indicates lower symmetry of 5-coordinated polyhedra of Sc in BaZrO<sub>3</sub>. By analyzing the difference in the symmetry of 5-coordinated polyhedra based on the DFT results, the large  $C_Q$  of BaZrO<sub>3</sub> seems to be originated from the large displacement of oxide ions due to the formation of the oxygen vacancy. From thermogravimetric analysis, Sc-doped BaZrO<sub>3</sub> incorporates more than 10 times larger amounts of proton than CaZrO<sub>3</sub>. These results indicate that hydration in these materials occurs to relax the local structure around the oxygen vacancy with large displacement of oxide ions by filling the vacancy with the hydroxide ion.

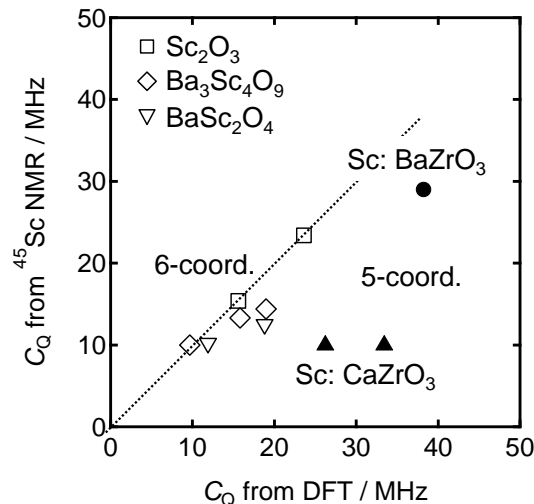


Figure 1 Quadrupole coupling constant,  $C_Q$ , of Sc sites obtained from DFT calculation and <sup>45</sup>Sc NMR measurements

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## DEFECT STRUCTURE OF BZCYYB17 AND THEORETICAL BEHAVIOR AND PERFORMANCE OF SOFC's With BZCYYb17 ELECTROLYTE

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**Key Words:** Proton conductors, Electrolytes, Defect chemistry, Theoretical approaches, Oxides

In this work, maximum power density of SOFC with BZCYYb17( $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-d}$ ) electrolyte as the function of thickness was calculated by integrating partial conductivities of charge carriers under various DC bias conditions at a fixed oxygen chemical potential gradient at both sides of the electrolyte. The partial conductivities were calculated by fitting various total conductivities in diverse thermodynamic conditions (temperature, partial pressure of oxygen and partial pressure of vapor) using equations from defect model. From the fitting, not only we can get the partial conductivities as a function of temperature, oxygen partial pressure and hydrogen partial pressure but also mobility of each carriers and reaction constant of oxidation and hydration. Spatial distribution of oxygen chemical potential and hydrogen chemical potential across the electrolyte were calculated based on Choudhury and Patterson's model by considering zero electrode polarization. At positive voltage conditions corresponding to SOFC and SOEC, the high conductivity region near n-type to p-type transition was expanded, but at negative cell voltage conditions, the low conductivity region near n-type to p-type transition was expanded. The current- voltage characteristics in different conditions with temperature and thickness dependence were calculated with vapor partial pressure of each electrode is 0.03, oxygen partial pressure of the cathode 0.21 and hydrogen partial pressure of the anode 0.97.

# REVERSIBLE WATER UPTAKE AND RELEASE OF PSEUDO-CUBIC TYPE $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ AT INTERMEDIATE TEMPERATURES

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**Key Words:** PCFCs;  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ ; Cathode;  $\text{H}_2\text{O}$  uptake; Intermediate temperature

Solid oxide fuel cells (SOFCs) based on oxide-ion conducting electrolytes possess several attractive advantages such as high energy conversion, low pollutant emission and fuel flexibility. However, SOFCs suffer from the high operating temperatures 800-1000 °C; such high temperature operations result in the increase of costs and lessened lifetimes of materials. Hence, there exists a strong demand to decrease the working temperature into intermediate temperature (IT) region below 600 °C. Proton conducting ceramic fuel cells (PCFCs) is a kind of promising IT-fuel cells operating at around 400-600 °C because of lower activation energies of proton conductivity than oxide-ion conductivity. Recently Choi et al [1] reported that PCFC with  $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$  electrolyte exceeds 500 mW cm<sup>-2</sup> at 500 °C, however, the performance still lags far behind the predicted values that is over 1.0 W cm<sup>-2</sup> at 500°C. There are two major challenges, one is big ohm resistance of Zr-rich Ba(Zr, Ce, Y)O<sub>3</sub> (BZCY) electrolyte, and the other one is lack of highly efficient cathode specially designed for PCFCs [2]. Since most of the cobaltite base cathodes are oxide-ion conductors, the mismatch of main ionic carriers between cathode and electrolytes limits the efficient cathodic reaction area into cathode-electrolyte-gas triple boundaries. Hence, it is motivated to develop cathode catalysts which exhibit sufficient proton conductivity in order to extend the efficient reaction zone and thus reduce cathode overpotentials and finally increase reaction efficiency. The protonic defects are incorporated into oxides via hydration reaction, whereas, many oxides do not have enough large hydration enthalpy [3-5] and thus, the reaction is less-pronounced at elevated temperatures.

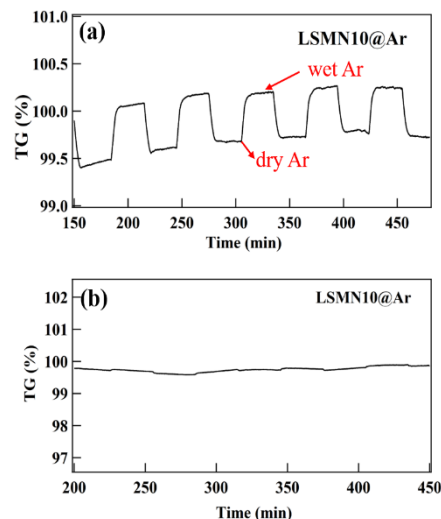
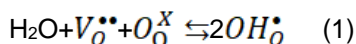


Figure 1 – Mass change of (a) PC-type LSMN and (b) R-type LSMN under dry and wet Ar at 415 °C

In this study, we report on the hydration behavior of cubic-perovskite-type  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$  (LSMN,  $x=0.0, 0.1$  and  $0.3$ ) in the intermediate temperature region. XRD patterns show that LSMN calcined at 800 °C (LSMN@800) is cubic (C) perovskite-type phase, while LSMN calcined at 1000 °C (LSMN@1000) is Rhombohedral (R) phase. Figure 1 (a) shows TG curves of C-type LSMN10 ( $x=0$ ) at 415 °C with switching repeatedly between dry and wet Ar, indicating the mass abruptly increases by exposed to wet Ar while, conversely, the mass intermediately decreases with introducing dry Ar. These results confirm that C-type LSMN10 are capable of reversible  $\text{H}_2\text{O}$  uptake/intake at the temperatures by the following defect reaction.



The amount of proton defects for LSMN10 can be calculated to be  $[\text{OH}]/[\text{LSMN}] \sim 0.12$ . Meanwhile, R-type LSMN10@1000 does not exhibit reversible mass changes at the temperature shown in Figure 1 (b), indicating that this does not cause the hydration. Now more detail structural and compositional analysis has been carried out.

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# MEASUREMENT OF THE ACTIVE WIDTH IN SR-DOPED LANTHANUM MANGANATE SOFC CATHODES USING NANO-CT, IMPEDANCE SPECTROSCOPY AND BAYESIAN CALIBRATION

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**Key Words:** Solid Oxide Fuel Cell, LSM, Nano-CT, Impedance Spectroscopy, Bayesian Calibration

Bayesian model-based analysis (BMA) is a method for producing quantitative models of complex physical systems through the comparison between models and experimental data. A model of a porous LSM cathode (symmetrical cell) was applied to impedance data and its parameters estimated via Bayesian calibration. X-ray computed tomography provided microstructural information for the model. The combination of model calibration and microstructural characterization enabled an estimate of the active thickness for a porous LSM electrode. The active width extended only a few nanometers from the surface, strongly suggesting that future models should explicitly resolve the space-charge region.

## EVALUATION OF THE HIGH TEMPERATURE SOLID OXIDE CELLS USING $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$

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Key Words: Electrodes, Thermochemical water splitting

The performance of the SOCs using  $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (LSCF1982) was characterized by I-V measurement and electrochemical impedance spectroscopy (EIS). The distribution function of relaxation times of EIS was used to analyze the polarization resistance of the cells. The fitting was performed using the appropriate equivalent circuit through DRT analysis. Furthermore, we co-electrolyzed  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to obtain  $\text{H}_2$  / CO syngas as well as water splitting. The composition of syngas was investigated by gas chromatography and controlled by varying in-let gas composition.

## OXYGEN NONSTOICHIOMETRY AND THERMODYNAMIC QUANTITIES OF PEROVSKITE-TYPE $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ( $x=0.2, 0.5, 0.8$ )

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**Key Words:** Defect chemistry, Thermodynamic properties, Theoretical approaches, Oxide-ion conductors, Mixed conductors

In this work, the defect structure analysis of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  ( $x=0.2, 0.5, 0.8$ ) was presented. Thermogravimetric measurements were performed to determine the change in oxygen nonstoichiometry ( $\Delta\delta$ ) with oxygen partial pressure ( $p\text{O}_2$ ) in  $10^{-19} \leq (p\text{O}_2/\text{atm}) \leq 0.21$  and temperature in  $750 \leq (T/^\circ\text{C}) \leq 900$  range.  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  showed a clear electronic stoichiometric point around  $\delta \approx 3-x/2$ . The relative partial molar enthalpy ( $h_o-h_o^\circ$ ) and entropy ( $s_o-s_o^\circ$ ) of oxygen were calculated from  $\delta$ - $p\text{O}_2$ - $T$  relation by using Gibbs-Helmholtz equation. The negative sign of  $h_o-h_o^\circ$  and  $s_o-s_o^\circ$  indicated that the incorporation of oxygen was an exothermic process and showed that the experimentally observed variations in  $h_o-h_o^\circ$  and  $s_o-s_o^\circ$  with  $\delta$  matched well with the statistical thermodynamic model proposed by Mizusaki<sup>[1]</sup>. The defect diagram analysis showed that in n-type regime  $\text{Fe}^{2+}$  concentration varied with  $(p\text{O}_2)^{-1/4}$  whereas in p-type regime  $\text{Fe}^{4+}$  concentration varied with  $(p\text{O}_2)^{1/4}$ .

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## HIGH RESOLUTION THERMOCHEMICAL STUDY OF PHASE STABILITY AND RAPID OXYGEN INCORPORATION IN $\text{YBaCo}_{4-x}\text{Zn}_x\text{O}_{7+\delta}$ 114-COBALTITES

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**Key Words:** calorimetry, 114-oxides,  $\text{YBaCo}_4\text{O}_7$ , thermodynamic stability, oxygen sorption.

The formation enthalpies of  $\text{YBaCo}_{4-x}\text{Zn}_x\text{O}_{7+\delta}$  ( $x = 0, 1$  and  $3$ ) oxides were measured by high temperature oxide melt solution calorimetry. All the studied oxides were shown to be thermodynamically metastable at low temperature with respect to a mixture of binary oxides  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}$  and  $\text{ZnO}$ . The tendency of cobalt to increase oxidation state under oxidizing conditions as well as significant bond valence sum mismatch for Ba and Y in 114-oxides are the main destabilizing factors. As a result, the studied 114-oxides are thermodynamically stable in air only at relatively high temperatures ( $> \text{ca. } 900^\circ\text{C}$ ) when  $\text{CoO}$  is stable. Oxygen absorption in  $\text{YBaCo}_{4-x}\text{Zn}_x\text{O}_{7+\delta}$  ( $x = 0, 1$  and  $3$ ) at  $350\text{--}400^\circ\text{C}$  was studied by calorimetry combined with precise oxygen dosing. Complex phase evolution in  $\text{YBaCo}_4\text{O}_{7+\delta}$  upon oxygen absorption was revealed. Several single and two phase fields were identified and a sketch of the phase diagram for  $\text{YBaCo}_4\text{O}_{7+\delta}$  was proposed. The calorimetric results support observations using in situ XRD. At the same time, thermochemical measurements were shown to have higher resolution with respect to the amount of oxygen absorbed by  $\text{YBaCo}_{4-x}\text{Zn}_x\text{O}_{7+\delta}$  sample under equilibrium conditions.

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## STRUCTURE AND PROPERTIES OF THE LAYERED PEROVSKITES IN SM-BA-CO-FE-O SYSTEM

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**Key Words:** crystal structure, defect structure, transmission electron microscopy, oxygen nonstoichiometry, conductivity

Perovskite oxide materials with the general formula of  $ABO_3$ , where A is an alkali earth or rare earth metals and B is transition metals, have attracted much attention as cathodes for solid oxide fuel cells because of their high electronic conductivity and fast mobility of oxygen ions. The introduction of  $Ba^{2+}$  and  $Ln^{3+}$  ions with significantly different radii into the A-sites leads to a formation of layered perovskite-type structures which have formed due to the cations' ordering in the alternating layers. Depending on the nature of rare earth and 3d metal, it was possible to obtain double  $LnBaM_2O_{6-\delta}$ , triple  $LnBa_2M_3O_{9-\delta}$ , or quintuple  $Ln_2Ba_3M_5O_{15-\delta}$  perovskites. The aim of the present work was studying the effect of Ln/Ba and Fe/Co ratio for the crystal and defect structure and properties of oxides in the Sm-Ba-Co-Fe-O system.

Polycrystalline samples of  $SmBaCo_{2-x}Fe_xO_{6-\delta}$  and  $Sm_{2-\varepsilon}Ba_{3+\varepsilon}Fe_{5-y}Co_yO_{15-\delta}$  were prepared by the glycine–nitrate synthesis. Final annealing was performed at 1100°C in air during 120h with intermediate grindings, followed by slow cooling down to room temperature at a rate of about 100°/h. The structural parameters were refined by the Rietveld method using the Fullprof-2008 software. Transmission electron microscopy studies were performed using FEI Tecnai G2 30 UT microscope operated at 300kV. The changes of oxygen content in complex oxides were measured by coulometric titration method as a function of temperature and oxygen partial pressure. The absolute value of oxygen content in the samples was determined using a direct reduction in the TG cell by hydrogen flow and red-ox titration. Thermal expansion of samples was studied using Netzsch DIL 402C dilatometer within the temperature range 25 – 1100°C in air. Total conductivity and Seebeck coefficient were measured simultaneously using a 4-probe technique.

The crystal structure of  $SmBaCo_{2-x}Fe_xO_{6-\delta}$  ( $0 \leq x \leq 0.5$ ) was described by the orthorhombic  $a_p \times 2a_p \times 2a_p$  cell ( $Pmmm$  sp. gr.), while  $SmBaCo_{2-x}Fe_xO_{6-\delta}$  ( $0.6 \leq x \leq 1.1$ ) crystallized in the tetragonal structure,  $a_p \times a_p \times 2a_p$  cell ( $P4/mmm$  sp. gr.). The crystal structure of single-phase  $Sm_{2-\varepsilon}Ba_{3+\varepsilon}Fe_{5-y}Co_yO_{15-\delta}$  ( $\varepsilon = 0$ ,  $y = 0.5-1.5$ ;  $\varepsilon = 0.125$ ,  $y = 0$ ) determined by XRD was described as cubic (sp. gr.  $Pm3m$ ). However, transmission electronic microscopy revealed that oxides possess tetragonal structure with 5-fold  $c$  parameter.

The defect structure of oxides with double perovskite structure was described using the model based on the simple cubic perovskite  $SmMeO_3$  ( $Me = Co, Fe$ ) as a reference state. Equilibrium constants and enthalpies of the point defects formation were refined. The concentrations of all defect species were calculated as functions of temperature and oxygen nonstoichiometry.

The temperature dependencies of total conductivity for  $SmBaCo_{2-x}Fe_xO_{6-\delta}$  and  $Sm_{2-\varepsilon}Ba_{3+\varepsilon}Fe_{5-y}Co_yO_{15-\delta}$  possess maxima at approximately 300–350°C in air. The partial substitution of iron for cobalt leads to a decrease in the conductivity value. Seebeck coefficient for all compounds reveals positive values within the entire temperature and oxygen partial pressure ranges that indicate predominant p-type conductivity.

The dependencies of electrical conductivity and Seebeck coefficient versus oxygen nonstoichiometry were discussed on the basis of the defect structure models. The values of activation energy for fixed oxygen content values were calculated.

This work was supported by the Russian Science Foundation (Grant № 18-73-00159)

### 3-POINT MEASUREMENT IN SOLID STATE DEVICES: (NOVEL) ARTEFACTS AND HOW TO AVOID THEM

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**Key Words:** Reference Electrode, 3 Point Measurements, No Artefacts, Solid State Devices

There are two common methods to measure the impedance response of only one electrode of a solid-state electrochemical cell, microelectrodes or a three-terminal configuration. In aqueous electrochemistry, three-terminal configurations are widely used, however, implementing this method in solid-state electrochemistry is highly non-trivial. This work summarizes, which method is most suitable for different applications. We show potential error sources and evaluate each of them quantitatively with special emphasis on their impact in thin film electrode measurements. Evaluation is done by means of finite elements analysis (FEA), electric circuit simulations and conducted measurements.

Three potential error sources were identified as particularly crucial factors: (i) Asymmetric sample cells (ii) short circuit currents across the reference electrode (RE), (iii) Especially for highly resistive electrode, coupling capacitances between the three electrodes.

These error sources can result in different measurement errors such as additional high frequency semicircles, additional low frequency semicircles, inductive loops and even more critical, erroneous electrode properties without indicating of additional features in the impedance spectrum.

We propose a novel sample geometry, the “wing geometry”, which was designed to minimize the measurement errors significantly, but still remains affordable and suitable for different applications.

## DISCUSSION ON ELECTRODE REACTION IN PARTIAL EQUILIBRIUM STATE BY EMF MEASUREMENTS

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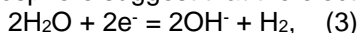
**Key Words:** Electrode reaction, Surface protonics, EMF, Partial equilibrium and LDH.

Nanocrystalline porous oxides and hydroxides are known to exhibit high proton and hydroxyl-ion conductivity in wet atmospheres. After a substantial number of challenges to improve the conductivity, it is well established that the surface protonic conduction is related to the hierarchical adsorbed water layer and the proton activity on the surface. However, details of electrode reaction for protonic conduction, which can be alternatively interpreted as a connection of ion formed by an electrode reaction to an ionic bridge, has never been discussed in previous studies. Recently, Stub et al. have measured the emf of the following water vapor concentration cell, Ag |porous-YSZ |Ag, under small water vapor gradients at a constant oxygen pressure, suggesting that the charge carrier is  $\text{H}_3\text{O}^+$  in higher relative humidity ( $\text{RH} > 0.6$ ) and a single proton hopping migration at lower RH region<sup>[1]</sup>. In their work, they assumed that two electrode reactions for  $\text{H}^+$  and  $\text{H}_3\text{O}^+$  shown in the following equilibria, are reversible even at low temperature around room temperature.

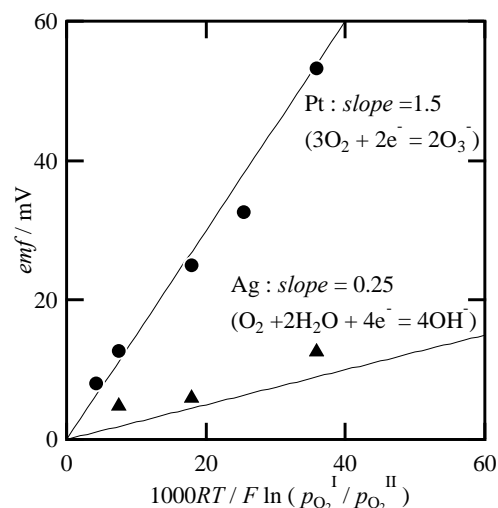


Inspired by their work, we carried out a series of experiments, to understand the relation between the electrode reaction and the emf of concentration cell; how the ion produced by the electrode reaction is connected to the ion migration process in the electrolyte. We employed both emf and AC impedance measurements to discuss the relationship between the electrode reaction and the charge carrier species. The values of emf was measured under a chemical potential gradients of oxygen, hydrogen or water vapor using compacted layered double hydroxide (LDH) as the electrolyte with Pt or Ag electrodes deposited on both sides of the samples by RF magnetron sputter.

Our emf measurements in hydrogen atmosphere suggest that the electrode reaction on Pt electrode,



is reversible because of fast hydrogen dissociation. Also, the H-D isotope effect is clearly observed in AC impedance measurements, indicating single proton hopping is the microscopic rate-limiting step in the ion transport process for macroscopic  $\text{OH}^-$  migration. Therefore, it is concluded that the  $\text{OH}^-$  produced by Eq. (3) eventually transports by the microscopic proton transfer from  $\text{H}_2\text{O}$  molecule to  $\text{OH}^-$ , as suggested theoretically in the previous report<sup>[2]</sup>. In oxidizing atmospheres, however, the emf value of oxygen concentration cell with Pt electrode is extraordinarily larger than the one with Ag electrode, as shown in *Figure 1*. The results suggest that oxygen molecule in the gas phase is apparently reduced to ozonide anion,  $\text{O}_3^-$  on Pt electrode rather than other common oxygen species, such as  $\text{O}^{2-}$ . From the H-D isotope effect estimated by an AC impedance in oxidizing atmosphere, the proton hopping transport on the surface of LDH is confirmed similarly to the one in reducing atmosphere. The extraordinary emf for Pt electrode is possibly due to slow ionic reactions between reduced oxygen inter-mediate on Pt electrode and protonic species on the basic surface of LDH owing to low availability of protonic carriers in the electrolyte. Further details on the relationship between the electrode reaction in the partial equilibrium state and the charge carrier species for various systems will be discussed at the presentation.



*Figure 1 EMF of oxygen concentration cell as a function of the oxygen partial pressure ratio. The slope reflects a reciprocal number of electrons per oxygen molecule in the reversible electrode reaction.*

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## DFT+U STUDIES INCLUDING SPIN-ORBIT COUPLING – A CASE STUDY FOR F-ELECTRONS IN PRASEODYMIUM-DOPED CERIA

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**Key Words:** Ceria, DFT+U, polaron, spin-orbit coupling

The mixed ionic electronic conductor Ceria exhibits not only a high concentration of Anti-Frenkel defects with high mobility, resulting in ionic conductivity of oxygen ions, but also enables an additional electronic conduction mechanism in form of small polaron hopping between the f-states of the cations. This promotes the reversible exchange of oxygen with the surrounding atmosphere and thus the oxygen storage capacity of the binary oxide  $\text{CeO}_{2-\delta}$ . The material has been established as a model system to describe both ionic and electronic transport processes in bulk material to gain deeper insights into the characteristics of polaron hopping and defect-defect interactions in mixed conductors. By introducing the redox active lanthanide Praseodymium to the Ceria host lattice, both electronic and ionic conductivities are increased in temperature and oxygen partial pressure regions where pure Ceria lacks of good performance. The redox properties of Pr-ions, shifting the equilibrium from  $\text{Pr}^{4+}$  to  $\text{Pr}^{3+}$  and forming oxygen vacancies, is key to understand the additional contribution to the total electrical conductivity and the enhanced catalytic activity. So far in literature, only the effect of  $\text{Pr}^{3+}$ -ions in the Ceria host lattice has been investigated by means of density functional theory. To complement these investigations with the impact of Pr-ions in both oxidation states, density functional theory was applied, including a Hubbard-U correction for electronic correlation in the f-states of both cations in  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ . A systematic study of spin polarization, antiferromagnetic coupling and spin-orbit interaction of the unpaired 4f-electrons was performed to investigate the influence of magnetic interactions on the description of localized polarons. The preferred localization of the excess electrons on Pr- rather than Ce-ions as well as the defect formation and configuration is discussed by analyzing the resulting energy levels and densities of states of the investigated ideal and defective super cells.



# ORIGIN OF THE SURFACE-ORIENTATION DEPENDENCE OF THE REDUCTION KINETICS OF ULTRATHIN CERIA

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**Key Words:** cerium oxide, PEEM, *operando*

Performance of catalytic redox reactions depends crucially on the oxygen storage and release capability of the catalyst and with that the catalyst's defect chemistry. Here, we show that the surface defect chemistry of cerium oxide, a prototypical reducible oxide, differs markedly between two surface terminations. The results are in good agreement with density functional theory calculations and provide important guiding factors for rational design of industrially relevant catalysts. The study is conducted by preparing (100) and (111) terminated nanoislands of cerium oxide next to each other on Cu(111). Leveraging the benefits of full-field imaging capability of photoemission electron microscopy (PEEM), we follow the structural and chemical properties of the nanoislands under reducing hydrogen atmosphere simultaneously and in situ. The results, summarized in Figure 1, directly reveal different overall reducibility that can be traced to equilibrium oxygen vacancy concentrations via a kinetic model. The density functional theory calculations provide further details regarding the equilibrium co-ordination of oxygen vacancies for both surface planes. Conjoining the two, the unique simultaneous nature of the PEEM-facilitated structure–activity relationship study allows us to separate the thermodynamics of reduction from the kinetics of oxygen exchange, revealing the fact that the difference in reducibility of the two surfaces of ceria is not determined by the kinetic rate constants of the reduction reaction, but rather by the equilibrium concentration of oxygen vacancies, an information that has not been provided by the isolated model system approach to date. Surprisingly, the reason for the different reducibilities is a purely geometric one: the creation of nearest neighbor oxygen vacancies.

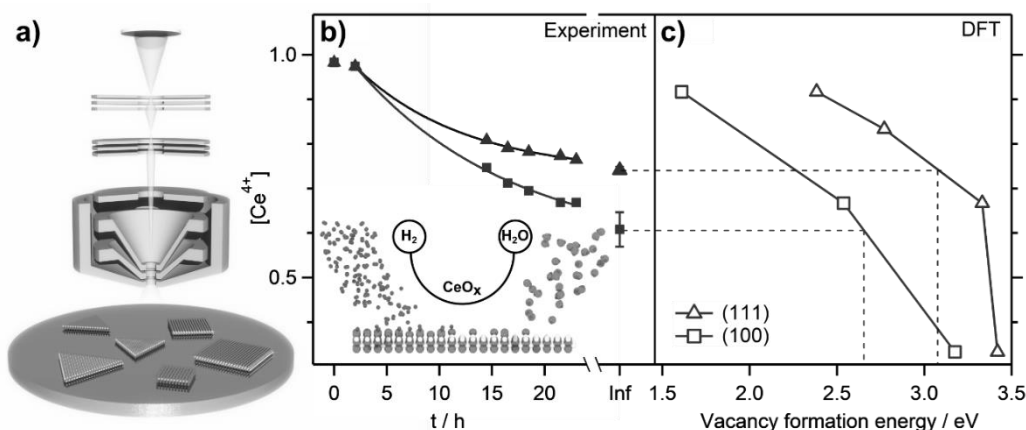


Figure 2 – (a) Schematics of the experimental layout. (b)  $\text{Ce}^{4+}$  content of ceria islands over time in hydrogen and fits to a kinetic model. (c) Oxygen vacancy formation energies as a function of  $\text{Ce}^{4+}$  content calculated using DFT from a 3ML slab.

# A HIGHLY ACTIVE AND DURABLE LANTHANUM STRONTIUM COBALT FERRITE CATHODE FOR INTERMEDIATE-TEMPERATURE SOLID OXIDE FUEL CELLS

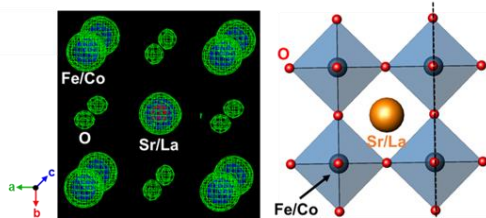
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**Key Words:** LSCF, SOFC, ECR, BVS, Stability

Solid oxide fuel cells (SOFCs) are promising techniques for high energy efficiency, fuel flexibility, and low pollutant emissions. For commercialization of SOFCs, it is required to decrease the operating temperature. At this intermediate temperature region, the cathodic polarization resistance significant due to the thermally activated oxygen reduction reaction (ORR). To compensate this, highly active cathode materials have been considered and lanthanum strontium cobalt ferrite (LSCF6428,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ) has been attracted as a cathode material for SOFCs because of its high mixed electronic and ionic conducting (MIEC) nature. However, one of the major concerns of LSCF6428 is the degradation during the long-term operation. Currently, Sr segregation has been reported as one of the major reasons for the LSCF degradation. In this study, we investigated LSCF2882 ( $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ) and compared with LSCF6428 as a SOFC cathode. X-ray diffraction (XRD) and Rietveld refinement were applied to analyze phase structures. By electrical conductivity relaxation (ECR) technique, Oxygen surface exchange coefficients ( $k_{\text{chem}}$ ) and chemical diffusion coefficients ( $D_{\text{chem}}$ ) of LSCF2882 were evaluated and we observed enhancements compare to LSCF6428. For interpretation of enhanced oxygen transport kinetics, we tried to visualize the interstitial oxygen conduction pathways and the bond valence sum (BVS) mapping method was utilized by Valence program. BVS mapping results show clearly demonstrating the 3D network of the interstitial pathways at 600°C in LSCF2882. Electrochemical performances were investigated by EIS (Electrochemical Impedance Spectroscopy) and single cell performance was also evaluated. In addition, long-term stability test was performed for over 500 hours. LSCF2882 showed better performances and it exhibited no degradation during the stability test.

**LSCF2882**



**LSCF6428**

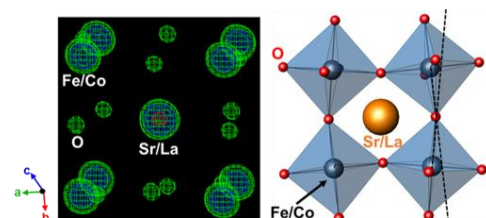


Figure 3 – Electron density map and unit cell structure of LSCF2882 and LSCF6428

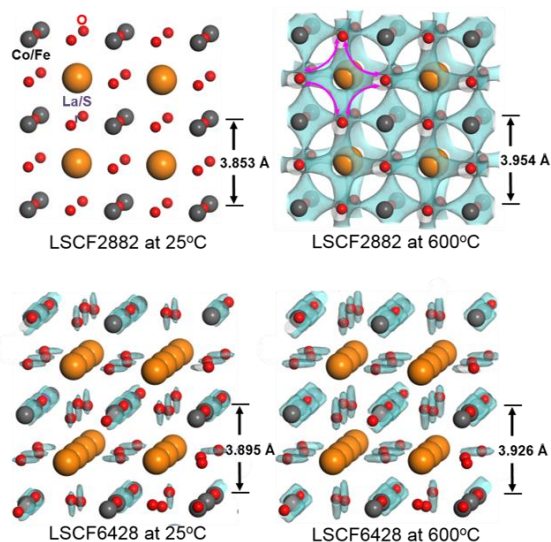


Figure 2 – bond valence sum (BVS) mapping results of LSCF2882 and LSCF6428

# HYDRATION THERMODYNAMICS OF PROTON-CONDUCTING PEROVSKITE $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$

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**Key Words:** perovskite, defects, proton conductor, hydration thermodynamics

The oxygen nonstoichiometry index  $\delta$ , i.e. number of oxygen vacancies per formula unit, in perovskite-type  $\text{BaCa}_{(1+y)/3}\text{Nb}_{(2-y)/3}\text{O}_{3-\delta}$  (BCNy) oxides can be tailored by varying the Ca–Nb ratio  $y$ , and equals  $\delta = y/2$ . These oxygen vacancies can be hydrated under humid atmosphere, providing nonstoichiometric BCNy oxides with good proton conductivity. It makes them promising materials for proton-conducting solid oxide fuel cell (SOFC) electrolytes and high-temperature humidity sensors. The present work aimed to partly address the lack of fundamental thermodynamic studies on BCNy by investigating the heat of low-temperature hydration-induced phase transition as well as the higher-temperature thermodynamics of hydration and related defect chemistry of BCN50 oxide.

BCN50 oxide was prepared via the standard ceramic technique from the high-purity  $\text{BaCO}_3$ ,  $\text{CaCO}_3$  and  $\text{Nb}_2\text{O}_5$ . Phase-purity of the as-obtained BCN50 powder was confirmed by means of X-ray diffraction (XRD) with 7000S diffractometer (Shimadzu, Japan) using Cu K $\alpha$  radiation. Calorimetric measurements were performed with an original heat-flux differential scanning calorimeter (DSC). Temperature-dependent equilibrium water content in BCN50 samples in dry ( $\log(p_{\text{H}_2\text{O}}/\text{atm}) \leq -3.5$ ) and wet ( $\log(p_{\text{H}_2\text{O}}/\text{atm}) = -1.67$ ) air was measured by thermogravimetry (TG) using CI Precision (UK) microbalances.

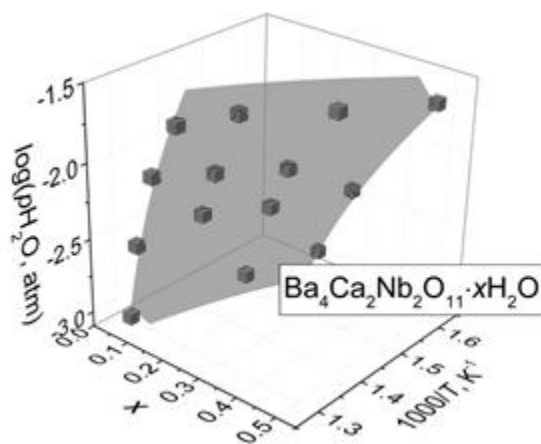


Figure 4 – The results of model analysis: points – experimental data [1], surface – fitted model

The defect structure model for BCN50 based on the single reaction of water uptake was discussed and successfully verified using the proton content dependencies,  $x(T, p_{\text{H}_2\text{O}})$ , at 623–773 K [1]. The values of the hydration enthalpy of cubic ( $Fm\bar{3}m$ ) BCN50, either measured directly or evaluated using the equilibrium  $p_{\text{H}_2\text{O}} - T - x$  data [1], were shown to be close to each other. The enthalpy of the cubic→monoclinic phase transition for  $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11} \cdot 0.92\text{H}_2\text{O}$  was calculated using calorimetrically measured low-temperature heat of hydration. As this transition introduces a degree of disorder, lowering the crystal lattice symmetry, its entropy,  $\Delta S_{\text{tr}}^0 = \Delta H_{\text{tr}}^0/T_{\text{tr}}$ , where  $T_{\text{tr}}$  is the phase transition temperature, should be positive, making the phase transformation enthalpy  $\Delta H_{\text{tr}}^0$  endothermic.

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## **IN SITU AND EX SITU STUDY OF CUBIC $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ TO DOUBLE PEROVSKITE $\text{LaBaCo}_2\text{O}_{6-\delta}$ TRANSITION**

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**Key Words:** Double perovskites, Disordered–ordered transition, Domain textured phases, Equilibrium phase diagram.

Double perovskites  $\text{REBaCo}_2\text{O}_{6-\delta}$  (RE – rare-earth element) have received great attention in past decades as promising materials for various electrochemical devices because of their high mixed ionic-electronic conductivity and catalytic activity for the reaction of oxygen reduction. Among these compounds, cobaltite  $\text{LaBaCo}_2\text{O}_{6-\delta}$  can serve as a good example of structural flexibility, since it is able to form either A-site disordered cubic “simple” perovskite or layered A-site ordered double perovskite. However, the exact limits of the thermodynamic stability of  $\text{LaBaCo}_2\text{O}_{6-\delta}$  double perovskite with respect to temperature ( $T$ ) and oxygen partial pressure ( $p\text{O}_2$ ) have not been determined so far. Furthermore, synthesis and study of selected properties of either cubic or layered  $\text{LaBaCo}_2\text{O}_{6-\delta}$  oxide were mostly of interest for researchers, whereas the transition from “simple” to double perovskite was not addressed in detail so far. At the same time, it is generally recognized that such transition significantly improves oxide ion transport in the perovskite-type oxides and, therefore, understanding this order-disorder transition is of key importance for successful development of new materials for practical application.

Therefore, the present work aims at providing some insights into the nature of the aforementioned order-disorder transformation of  $\text{LaBaCo}_2\text{O}_{6-\delta}$ , as well as into thermodynamic stability of both ordered and disordered phases, using a set of complementary techniques such as transmission electron microscopy, *in situ* X-ray diffraction and solid state coulometric titration.

As a result, formation of complex domain textured intermediate products during the phase transition “ordered  $\text{LaBaCo}_2\text{O}_{6-\delta}$  – disordered  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ ” was revealed. These products were found to exhibit strong affinity to oxygen and fast oxygen exchange with ambient atmosphere even at temperature as low as 70 °C. This particularity seems to provide a unique possibility to develop a new class of advanced materials for IT SOFCs, ceramic membranes and catalysis.

The thermodynamic stability limits of the cubic and double perovskites were determined as  $\log(p\text{O}_2) = f(1/T)$  dependencies. The stability diagram of the  $\text{LaBaCo}_2\text{O}_{6-\delta}$  –  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  system was plotted as a result. Oxygen nonstoichiometry of the thermodynamically stable cubic perovskite  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  was measured as a function of  $p\text{O}_2$  in temperature range between 1000 and 1100 °C using coulometric titration technique.

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## HEAT INCREMENTS AND OXIDATION ENTHALPIES OF (Y,Pr,Gd)BaCo<sub>2</sub>O<sub>6-δ</sub> DOUBLE PEROVSKITES

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Complex oxides (Y,Gd,Pr)BaCo<sub>2</sub>O<sub>6-δ</sub> attracts researchers' attention due to it are promising materials for cathodes for solid state fuel cells. However, fundamental thermodynamic properties of these double perovskites such as heat increments, heat capacity and enthalpy of oxidation are not investigated so far.

Powder samples of (Y,Gd,Pr)BaCo<sub>2</sub>O<sub>6-δ</sub> were prepared using glycerol–nitrate technique. Phase composition of investigated double perovskites was controlled by X-ray powder diffraction. Then samples with composition GdBaCo<sub>2</sub>O<sub>5.51</sub>, PrBaCo<sub>2</sub>O<sub>5.77</sub>, YBaCo<sub>2</sub>O<sub>5.33</sub> were prepared by slowly cooling with speed rate 100 K/h, whereas sample YBaCo<sub>2</sub>O<sub>5.0</sub> was prepared by annealing at 1373 K and quenching.

Enthalpy increments of all as-prepared samples were measured by high temperature drop-calorimetry method on the SETARAM MHTC 96 calorimeter. Since YBaCo<sub>2</sub>O<sub>6-δ</sub> is stable only above 1123 K in air, calorimetry measurements were carried out in region 1123 ≤ T, K ≤ 1323. Oxidation enthalpies of (Gd,Pr)BaCo<sub>2</sub>O<sub>6-δ</sub> were measured by means of DSC sensors of MHTC 96 calorimeter at 1173K. Oxidation enthalpy of YBaCo<sub>2</sub>O<sub>6-δ</sub> was calculated from heat increments measurements. Obtained data allow us to calculate a heat capacity dependency from temperature for these compounds.

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