



## **Beneficial Effect of Surface Decorations on the Surface Exchange of Lanthanum Strontium Ferrite and Dual Phase Composites**

**Ovtar, Simona; Søgaard, Martin; Song, Jia; Hendriksen, Peter Vang**

*Published in:*  
Electrochemical Society. Meeting Abstracts (Online)

*Publication date:*  
2016

*Document Version*  
Early version, also known as pre-print

[Link back to DTU Orbit](#)

*Citation (APA):*  
Ovtar, S., Søgaard, M., Song, J., & Hendriksen, P. V. (2016). Beneficial Effect of Surface Decorations on the Surface Exchange of Lanthanum Strontium Ferrite and Dual Phase Composites. Electrochemical Society. Meeting Abstracts (Online), MA2016-02.

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### **Beneficial Effect of Surface Decorations on the Surface Exchange of Lanthanum Strontium Ferrite and Dual Phase Composites**

S. Ovtar, M. Søggaard (Technical University of Denmark), J. Song (University of Twente), and P. V. Hendriksen (Technical University of Denmark)

#### **Abstract Text:**

Perovskites within the (La,Sr)(Fe,Co)O<sub>3</sub> class of materials show variations in the oxygen stoichiometry depending on temperature and oxygen activity and can potentially be used as catalysts, electrodes in high-temperature solid oxide fuel cells, gas sensors or for oxygen transport membranes. These perovskites possess a mixed ionic and electronic conductivity (MIEC), which can be highly beneficial for the processes on oxygen electrode surfaces. The oxygen transport through a MIEC is determined by the rate of the oxygen exchange over the gas-solid interface and the diffusivity of oxide ions and electrons (or holes) in the bulk. The oxygen exchange process over the surface in general involves several reaction steps, O<sub>2</sub> adsorption, dissociation, charge transfer and incorporation of ionic species. The Co-free end member of the material class; LSF (e.g. (La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3-δ</sub>) is fairly low cost and chemically stable in both mildly reducing and oxidizing atmosphere. The electronic conductivity is excellent (283 S/cm at 800 °C) but the ionic conductivity especially at low temperature is limited (0.014 S/cm, 800 °C). Due to these properties the material is a candidate for use in composite membranes in combination with a better ionic conducting material like CGO. Such systems are also excellent model systems for fundamental studies of the oxygen exchange process.

The aim of this study is to characterize the oxygen transport properties of a dual-phase composite system as a function of temperature, and to elucidate the origin of the enhancement of the surface exchange reaction that has been reported to occur in such systems<sup>1</sup> by increasing the amount of ionic conductor. Additionally, the effect of surface decorations (desired) and impurities (undesired) on the surface exchange was studied to illustrate the importance of controlled conditions for the sample preparation and measurements.

Electrical Conductivity Relaxation (ECR) was used to study the surface exchange reaction and the oxygen ion diffusion of single phase (La<sub>0.6</sub>Sr<sub>0.4</sub>)<sub>0.98</sub>FeO<sub>3-δ</sub> and dual phase composites of (La<sub>0.6</sub>Sr<sub>0.4</sub>)<sub>0.98</sub>FeO<sub>3-δ</sub> – Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (LSF-CGO). From the relaxation curves, fitted by using Fick's Laws of diffusion with appropriate boundary conditions, both the oxygen surface exchange coefficient ( $k_{ex}$ ) and the oxygen chemical diffusion coefficient ( $D_{chem}$ ) was derived.

The results of ECR clearly show that the CGO surface is involved in the surface exchange reactions on the composite and that by increasing the fraction of CGO the surface exchange is significantly enhanced. The involvement of CGO in the surface exchange can arise from fast exchange in the triple phase boundaries and/or the spillover of oxygen ions from LSF to CGO, where they incorporate. Additional effects can also originate from the fact that LSF scavenges impurities from CGO and therefore activate the CGO surface for the surface exchange reaction as proposed by Druce et al. <sup>2</sup>. This was separately studied by coating of the surface of the single phase LSF and the composite with different elements/oxides regarded as potential impurities. However, opposite to the trivial anticipation a strong positive influence of secondary phases (not normally considered to be good oxygen reduction catalysts) on the surface exchange coefficient was observed. For example depositing CaO/CaCO<sub>3</sub> on the surface led to an enhancement of the oxygen incorporation rate for 3.4 times at 750 °C.

The study concludes that the formation of a composite of MIEC and ionic conductor and controlled coating with a range of secondary phases on the surface (e.g. CaO, ...) is highly beneficial for the oxygen reduction process.

1. Hu, B.; Wang, Y.; Xia, C., *J. Power Sources* **2014**, *269*, 180-188
2. Druce, J.; Kilner, J. A., *J. Electrochem. Soc.* **2014**, *161*, F99-F104.

**Symposium Selection:** L03 - Electrode Processes 11

**Submitter's E-mail Address:** simov@dtu.dk  
**Preferred Presentation Format:** Oral

First Corresponding Author

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Dr Simona Ovtar  
**Affiliation(s):** Technical University of Denmark  
**Address:**  
Frederiksborgvej 399  
Roskilde,  
Denmark  
**Phone Number:** DK-4000  
**E-mail Address:** simov@dtu.dk

Second Author

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Dr Martin Søggaard  
**Affiliation(s):** Technical University of Denmark  
**Phone Number:**  
**E-mail Address:** mso@meneta.dk

Third Author

---

Mr Jia Song  
**Affiliation(s):** University of Twente  
**Phone Number:**  
**E-mail Address:** sonjustc@gmail.com

Fourth Author

---

Prof. Peter Vang Hendriksen  
**Affiliation(s):** Technical University of Denmark  
**Phone Number:**  
**E-mail Address:** pvhe@dtu.dk

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