



## STRUCTURE, STABILITY, AND TRANSPORT PROPERTIES OF NEW COMPOSITE MATERIALS FOR HYDROGEN ENERGY

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### Abstract

Proton conducting oxides can be applied in various electrochemical devices such as gas sensors, hydrogen pumps, membrane reactors, and Protonic-Ceramic Fuel Cells (PCFC). This has resulted in increased attention for these materials, especially in terms of PCFC application due to its lower operating temperature compared with traditional Solid Oxide Fuel Cells (SOFC) with an oxygen conducting electrolyte. Besides, higher fuel utilization is achievable for PCFC when hydrogen used as fuel, and the utilization efficiency of hydrocarbon fuel is significantly higher.

In this work the well-known proton-conducting oxide  $\text{La}_{0.9}\text{Sr}_{0.1}\text{ScO}_{3-\delta}$  (LSS) is modified by the introduction of transition metal cations into a Sc sublattice in order to enhance the electronic conductivity of the material. Introduced cations of transition metal are selected on the basis of their ion radii and the variety of oxidation state, thus the compositions under study are  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{1-x}\text{Me}_x\text{O}_{3-\alpha}$  (LSSMe) (where Me is Ti, Fe, Co, Ni, or Mo). The composite materials, based on the ceramic matrix of the modified proton-conducting electrolyte LSSMe are studied in terms of their physical properties and electrochemical performance.

### Composition of the ceramic matrix

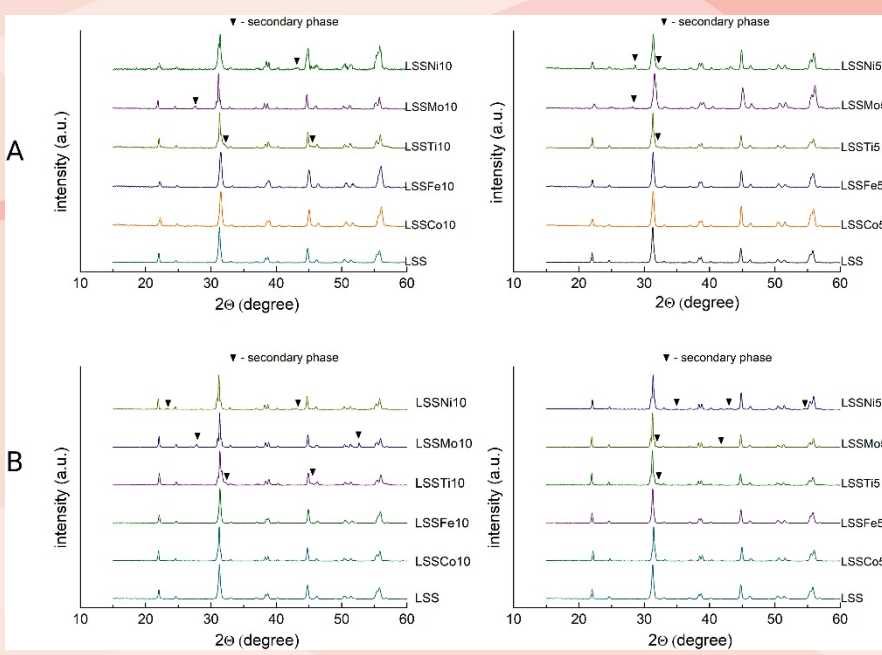


Fig. 1. X-ray diffraction patterns of LSSMe5 (right) and LSSMe10 (left) recorded at room temperature. A - after calcination in air. B - after calcination in hydrogen.

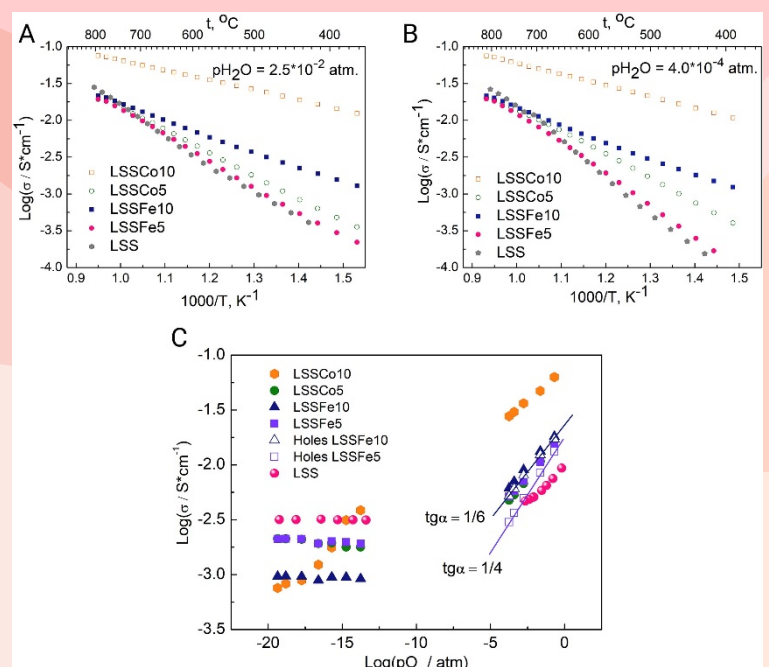


Fig. 2. Temperature dependence of LSSCo and LSSFe conductivity in wet air ( $\text{pH}_2\text{O} = 2.5 \cdot 10^{-2}$  atm) - A and dry air ( $\text{pH}_2\text{O} < 4.0 \cdot 10^{-4}$  atm) - B. Total conductivity of LSSMe as a function of  $\text{pO}_2$  in wet atmosphere ( $\text{pH}_2\text{O} = 2.5 \cdot 10^{-2}$  atm) at 800 °C - C.

### Composite system $\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{1-x}\text{Me}_x\text{O}_{3-\alpha}$ - $\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$

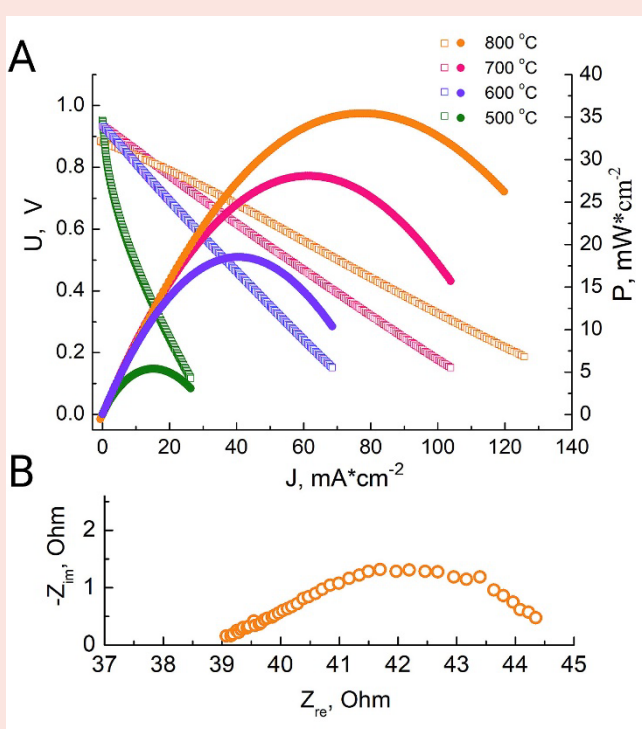


Fig. 3. A - I-V and power density curves. B - impedance spectrum of the LSSCo10-LNF, air+2.5%  $\text{H}_2\text{O}$ |LSS|LSSCo10-Ni,  $\text{H}_2$ +2.5%  $\text{H}_2\text{O}$  protonic ceramic fuel cell.

Fig. 4. Distribution of relaxation times (DRT) curves at 650 °C of LSSMe-LNF|LSS|LSSMe-LNF cell.

### Composite system $\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{1-x}\text{Co}_x\text{O}_{3-\alpha}$ - $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$

The  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{1-x}\text{Co}_x\text{O}_{3-\alpha}$ - $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$  (LSSCo-LCS) composite materials were obtained by mechanical mixing of single-phase powders of proton-conducting and electron-conducting materials in a planetary mill, followed by pressing and sintering. The components of the composites were  $\text{La}_{0.9}\text{Sr}_{0.1}\text{ScO}_{3-\delta}$  (LSS),  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta}$  (LSSCo10), and  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_{3-\delta}$  (LSC) as an electron-conducting phase. The powders were mixed in three different weight ratios of 60 by 40 LSSCo to LSC; 50 to 50 LSSCo10 to LSC and 40 to 60 LSSCo10 to LSC.

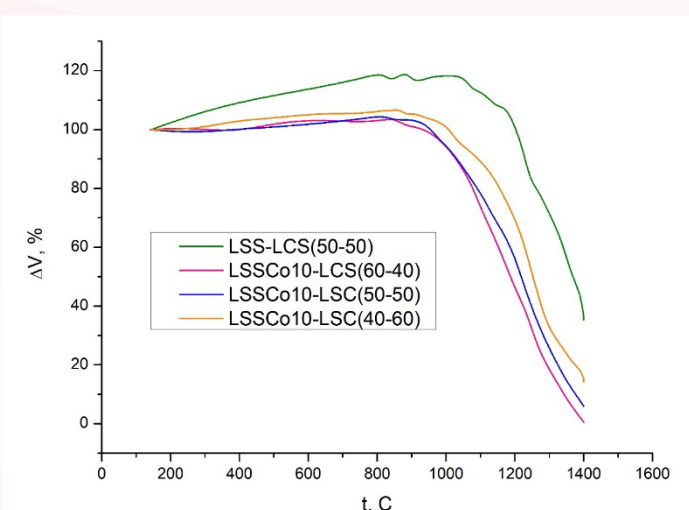


Fig. 5. Sintering curves of LSS-LCS samples (50-50); LSSCo10-LCS (60-40); LSSCo10-LCS (50-50) and LSSCo10-LCS (40-60) obtained with a high temperature microscope

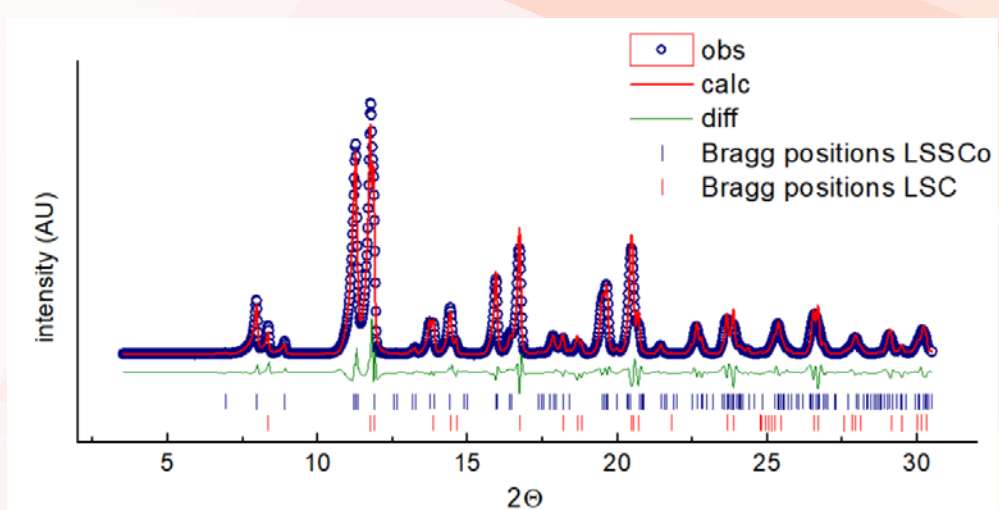


Fig. 6. Results of Rietveld refinement of composite sample LSSCo10-LCS (40-60) sintered at 1300 °C

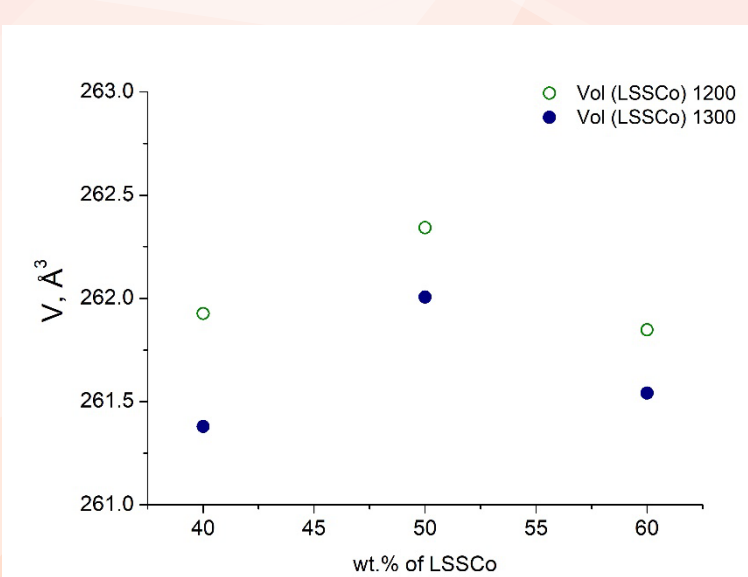


Fig. 7. Dependence of the lattice volume of the LSSCo phase on the composite composition and sintering temperature.

### Conclusion

In this work, we modified a well-known proton-conducting electrolyte based on  $\text{LaScO}_3$  for its application as a mixed ionic and electronic conducting electrode material. It was shown that among compositions of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{1-x}\text{Me}_x\text{O}_{3-\alpha}$  (LSSMe) (where Me is Ti, Fe, Co, Ni, or Mo and  $x = 0.05$  or  $0.10$ ) only Co and Fe containing samples were single phased in both oxidizing and reducing atmospheres. It was shown that  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{0.9}\text{Co}_{0.1}\text{O}_{3-\alpha}$  has the highest value of conductivity and the best electrochemical performance in composite cathodes  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{1-x}\text{Me}_x\text{O}_{3-\alpha}$ - $\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$ . The possibility of the creation of the  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{1-x}\text{Co}_x\text{O}_{3-\alpha}$ - $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$  composite electrodes is studied. It is shown that the sinterability increases along with the amount of the LSSCo phase. The lattice volume of the LSSCo phase decreases with the increase in sintering temperature, which means that Co diffuses from LCS phase into LSSCo

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