

Control of Oxygen Non-Stoichiometry in $\text{La}_x\text{A}_{1-x}\text{Mn}_y\text{B}_{1-y}\text{O}_{3+\delta}$ Perovskites for SOFC Applications

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Introduction

The Solid Oxide Fuel Cells (SOFC) are the most efficient in the conversion of chemical to electric energy among all fuel cell types [1]. In addition, their high operation temperature allows the use of inexpensive catalysts as electrodes and a high tolerance to gaseous impurities. The cathode of the SOFCs is typically made of strontium substituted lanthanum manganite (LSM). This material allows electronic conduction owing to its p-type semiconductor properties and is a good oxygen activator and oxide ion conductor due to the redox properties of the Mn cation and the oxygen vacancies (non-stoichiometry) entrained by the partial substitution of the lanthanum [2].

In the present work two series of La- substituted and Mn-substituted perovskites were studied by using complementary methods to assert their suitability as cathode materials for SOFC. Lanthanum was partially substituted with Sr, Ba, Cs and K, to investigate the effects of the valence and ion radius of the A-site cation. Manganese was partially substituted with Cu, Ni, and Zn cations with lower oxidation states and different reducibility than Mn.

Materials and Methods

The perovskites were prepared by using metal nitrates as precursors in appropriate ratio [2-4]. Calculated amounts of dried nitrates were dissolved in distilled water and glucose was added to enhance the surface area of the catalysts. The solution was evaporated to dryness and the solid material was calcined at 750°C in air for 6 h. La_2O_3 (Aldrich), MnO_2 (Merck) CuO , NiO , and Mn_2O_3 (prepared by decomposition of metal nitrates at 750°C) were taken for comparison.

The oxides were subjected to temperature programmed reduction and re-oxidation to investigate their reducibility and oxygen stoichiometry. The catalytic activity in hydrogen oxidation was tested in a gradientless recirculation reactor as a measure of the rate and amount of oxygen activation in dynamic conditions.

Results and Discussion

Fig. 1 shows the TPR profiles of the partial substituted perovskites $\text{La}_{0.8}\text{A}_{0.2}\text{MnO}_{3+\delta}$ (A = Sr, Ba, Cs, and K) (Fig. 1A) and $\text{LaMn}_{0.8}\text{B}_{0.2}\text{O}_{3+\delta}$ (B = Cu, Ni, and Zn) (Fig. 1B) as compared to the parent LaMnO_3 . The non-substituted perovskite displays an oxidative non-stoichiometry $\delta=0.16$, meaning that a part of manganese is in the oxidation state (4+). All A-site substituted perovskites show a higher reducibility than LaMnO_3 , especially when substitution was made by alkali. At the same time the lattice oxygen excess is diminished, especially for the earth-alkali substituted perovskites ($\delta=0.07$ for Sr). Both increased reducibility and decreased oxygen excess point to a higher mobility of the lattice oxygen, which are paramount for a cathodic material. In the B-substituted series the Cu containing perovskite is particularly reducible and presents a low oxygen non-stoichiometry of $\delta=0.04$. By

increasing the copper substitution at 50% the stoichiometry becomes $\delta=-0.16$, that means, the oxide is oxygen deficient. In the copper substituted oxides the oxygen mobility seems to be the highest.

The activity in hydrogen oxidation shows the following trends: A) $(\text{La,Sr}) > (\text{La,Ba}) \geq (\text{La}) \cong (\text{La,K}) \cong (\text{La,Cs})$; B) $(\text{Mn,Cu}0.2) \gg (\text{Mn,Cu}0.5) > (\text{Mn}) > (\text{Mn,Ni}) \cong (\text{Mn,Zn})$. This indicates that a large mobility and reducibility does not necessarily mean a large rate of oxygen activation in dynamic regime. From both points of view oxygen mobility and oxygen activation, the (La,Sr) and (Mn,Cu) perovskites seem to be the best. The oxidation activity of $\text{LaMn}_{0.8}\text{Cu}_{0.2}\text{O}_{3+\delta}$ is about three times larger than that of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$, and the latest is about two times more active than LaMnO_3 . In light of these results it seems that the copper substituted lanthanum manganite could be a better cathode material than the established LSM.

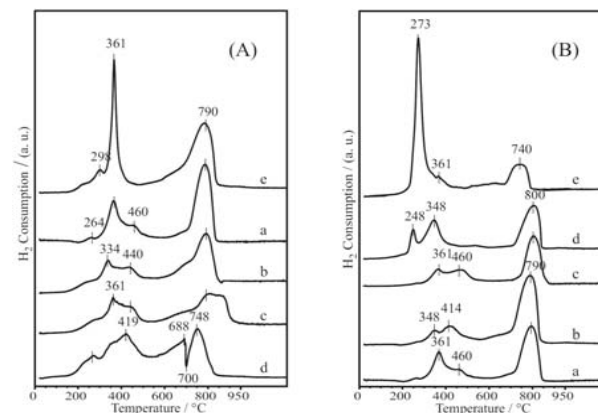


Figure 1: The TPR patterns of A) La-substituted (a-La; b-La,Sr; c-La,Ba; d-La, K; e-La,Cs) and B) Mn-substituted (a-Mn; b Mn,Ni; c-Mn,Zn; d-Mn,Cu0.2; e-Mn,Cu0.5) perovskite LaMnO_3 .

Significance

The fundamental study presented here shows the mechanism of controlling the oxygen mobility and oxygen activation rate on perovskitic lanthanum manganite by the appropriate substitution of the A-site or B-site cation. The results indicate that copper substituted lanthanum manganite could be a much better cathode material than the lanthanum strontium manganite (LSM) in the solid oxide fuel cells.

References

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