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Effect of A-site dopant on hydrogen La_{1-x}M_xAl_{1-y}Mn_y (M=Na and Sr) perovskite oxides for thermochemical water splitting applications

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The study focuses effect of A-site substitution on the structural properties of $La_xNa_{1-x}Al_yMn_{1-y}-La_xSr_{1-x}Al_yMn_{1-y}$ (x=0.2, 0.4, 0.6, 0.8, y=0.2, 0.4, 0.6, 0.8) (Na-Sr) perovskite oxides were synthesized by the Pechini method to observe the effect of structural properties on hydrogen production. Na was used as the A-site dopant, which was studied for the first time [1]. 8 different compositions in the LNAMn, LSAMn oxide family evaluated by the water splitting test. Figure 1 shows that oxygen production capacities of given perovskite oxides.



Figure 1. The O₂ production rate-time profiles a) LNAMn2837 and LSAMn2837 b) LNAMn4655 and LSAMn4655 c) LNAMn6473 and LSAMn6473 d) LNAMn8291 and LSAMn8291 perovskite oxides.

The areas under the curves are also the total O_2 gives the amount of formation. All the studies carried out O_2 formation were determined in the compositions, Table 1.

Table 1.O2 production in LNAMn and LSAMn perovskiteoxides.

Perovskite Oxide	First O ₂ Temperature (°C)	O2 Amount(µmol)	
LNAMn2837	600	159	
LNAMn4655	880	328	
LNAMn6473	1100	340	
LNAMn8291	900	374	
LSAMn2837	1350	696	
LSAMn4655	1330	642	
LSAMn6473	1400	494	
LSAMn8291	1400	641	

According to these data, it was determined that more O_2 production was observed in the Sr-doped perovskites compared to Na-doped ones. than the Na ones. Similarly, the H₂ production capacities were determined at 800°C by the thermochemical water splitting test, Figure 2.



Figure 2. The H_2 production rate-time profiles a) LNAMn2837 and LSAMn2837 b) LNAMn4655 and LSAMn4655 c) LNAMn6473 and LSAMn6473 d) LNAMn8291 and LSAMn8291 perovskite oxides.

 H_2 production was observed in all the compositions considered. All of the studies carried out H_2 formation was determined in the compositions, Table 2.

Table 2. Values obtained during H₂ formation from perovskite powders.

Perovskite Oxide	H_2	H_2/O_2	H_2/O_2
	Amount(µmol)	(µmol/g)	(%)
LNAMn2837	54	0.33	67.92
LNAMn4655	30	0.09	18.29
LNAMn6473	26	0.07	15.29
LNAMn8291	29	0.07	15.51
LSAMn2837	84	0.12	24.14
LSAMn4655	254	0.39	79.13
LSAMn6473	164	0.33	66.40
LSAMn8291	218	0.34	68.02

Redox activities for the compositions were obtained as approximately 79%, 66%,68%, and 67% for LSAMn4655, LSAMn6473, LSAMn8291, and LNAMn2837, respectively. It has been observed that Sr^{2+} element, which is the A-site doping element, plays a dominant role on hydrogen production.

References

[1]Scheffe, Jonathan R., David Weibel, and Aldo Steinfeld. 2013. "Lanthanum-Strontium-Manganese Perovskites as Redox Materials for Solar Thermochemical Splitting of H2O and CO2." *Energy and Fuels* 27 (8): 4250–57. https://doi.org/10.1021/ef301923h.



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