

LSMA-LCMF Dual Perovskite Oxides for Hydrogen Production

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Perovskite oxides are attracting attention as they can be used in thermochemical water splitting (TWS) reactions because they allow compositional diversity and provide higher structural stability. However, they need improvement in terms of structural stability, high reaction kinetics, and high stability during the thermal cycles [1].

For this purpose, it was aimed to improve the hydrogen production rate (>80%) with the existence of hetero-interfaces and preserve stability during the redox cycles. It is known that the hydrogen production capacity of perovskite oxides decreases dramatically (40%-80 %) in initial cycles [2].

In this study, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.6}\text{Al}_{0.4}\text{O}_3$ -LSMA6464 perovskite oxide and $\text{La}_{1-x}\text{Ca}_x\text{Mn}_y\text{Fe}_{1-y}\text{O}_3$ -LCMF (Ca=0.4-0.8, Al=0.4-0.8) families were selected for the dual-perovskites where LSMA6464 perovskite oxide is already one of the promising compositions for the TWS [3]. A total of 3 perovskite oxides, LCMF6482, LCMF6464, and LCMF6446, were selected from the LCMF family to create a hetero-interface. These compositions were then evaluated in thermochemical redox reactions ($T_{\text{red}} \sim 1400^\circ\text{C}$, $T_{\text{ox}} \sim 800^\circ\text{C}$). The H_2 production curves obtained from LSMA6464-LCMx compositions are given in Figure 1 and the calculated H_2 production rates and capacities are shown in Table 1.

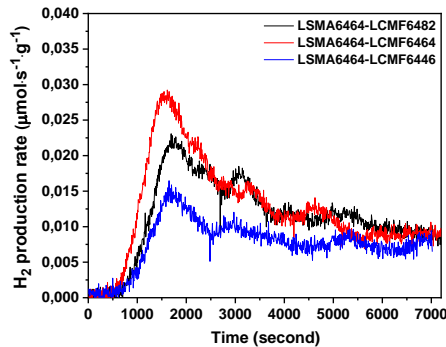
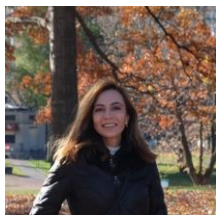


Figure 1. H_2 production curves obtained at 800°C from dual perovskites of LCMF6482, LCMF6464, LCMF6446 with LSMA6464.

LSMA6464 has the highest hydrogen production with a first-cycle production value of $257.18 \mu\text{mol/g}$. LCMF6482, LCMF6464, and LCMF6446 had the hydrogen production rate with a value of $39.09 \mu\text{mol/g}$, $37.21 \mu\text{mol/g}$, and $59.51 \mu\text{mol/g}$, respectively.



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Table 1. H_2 production values obtained from compositions in the LSMA6464-LCMx oxide family in the water splitting test at 800°C .

LSMA6464-LCMx	Highest H_2 production rate ($\mu\text{mol/g.s}$)	Time to reach the highest H_2 production (min)	Total H_2 production ($\mu\text{mol/g}$)
LSMA6464-LCMF6482	0.0232	28	83.92
LSMA6464-LCMF6464	0.0291	27	93.98
LSMA6464-LCMF6446	0.0164	27	53.49

Among the dual-perovskite, LSMA6464-LCMF6464 was the composition with the highest hydrogen production, with a first cycle production value of $93.98 \mu\text{mol/g}$. It was followed by LSMA6464-LCMF6482 and LSMA6464-LCMF6446 with $83.92 \mu\text{mol/g}$ and $53.49 \mu\text{mol/g}$, respectively.

Although there was an improvement in the individual hydrogen production capacity of LCMF perovskite oxides, it was still insufficient to be able to use in TWS. The hydrogen production was not sufficient. Here, it can be commented that the hetero-interface approach has an effect on hydrogen production.

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References

- [1] J.R. Scheffe, A. Steinfeld, Oxygen exchange materials for solar thermochemical splitting of H_2O and CO_2 : a review, *Mater Today*, 17, 2014
- [2] Abanades, Stéphane, Legal, A., Cordier, A., Peraudeau, G., Flamant, G., Julbe, A. 2010a. "Investigation of reactive cerium-based oxides for H_2 production by thermochemical two-step water-splitting". *Journal of Materials Science*, 45(15), 4163-4173.
- [3] Şanlı SB, Pişkin B, Effect of B-site Al substitution on hydrogen production of $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{1-x}\text{Al}_x$ ($x=0.4, 0.5$ and 0.6) perovskite oxides, *International Journal of Hydrogen Energy*, 2022