

## Supporting Information

# Cation Synergy in Sr and Al substituted LaMnO<sub>3</sub> during Solar Thermochemical CO<sub>2</sub> Splitting

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## Figures

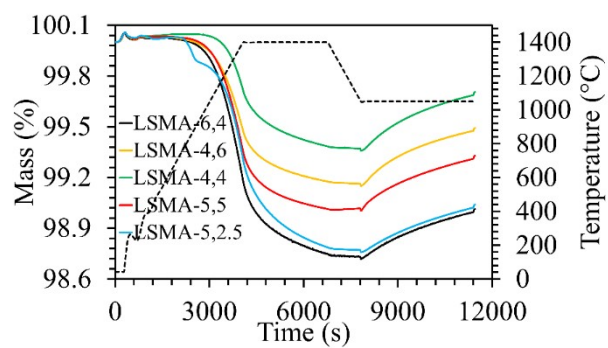


Figure S1. Mass variation profiles of  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  perovskite oxygen carriers during one redox cycle comprising thermochemical reduction and subsequent  $\text{CO}_2$  splitting. The dashed line represents the corresponding temperature variation.

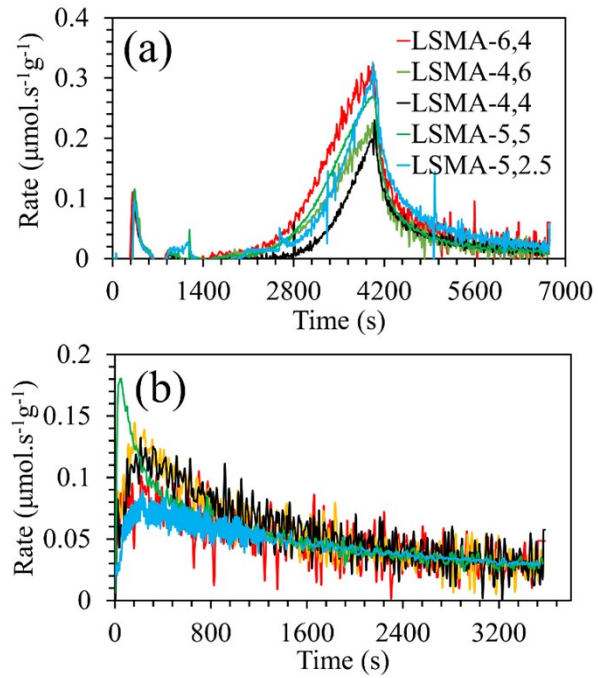


Figure S2. Reaction rates for (a) O<sub>2</sub> evolution and (b) CO evolution derived from mass variation during thermochemical reduction and CO<sub>2</sub>-induced re-oxidation of La<sub>x</sub>Sr<sub>1-x</sub>Mn<sub>y</sub>Al<sub>1-y</sub>O<sub>3</sub>.

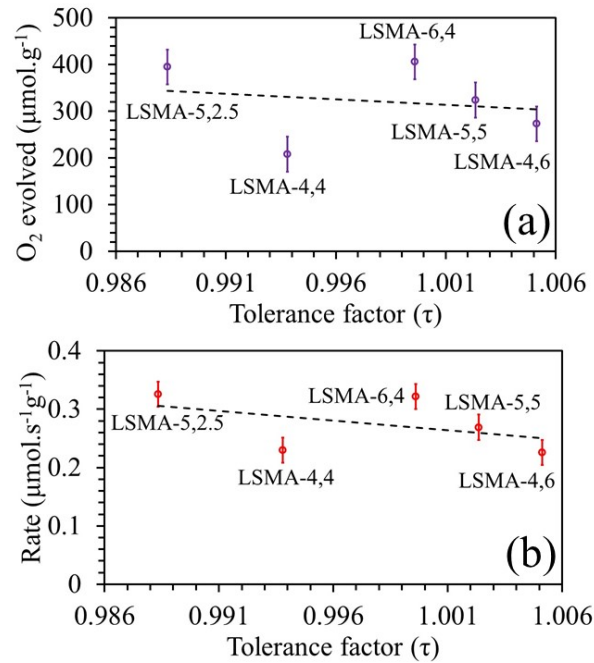


Figure S3. Amounts of  $O_2$  evolved (a) and reduction rates (b) as a function of tolerance factor for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

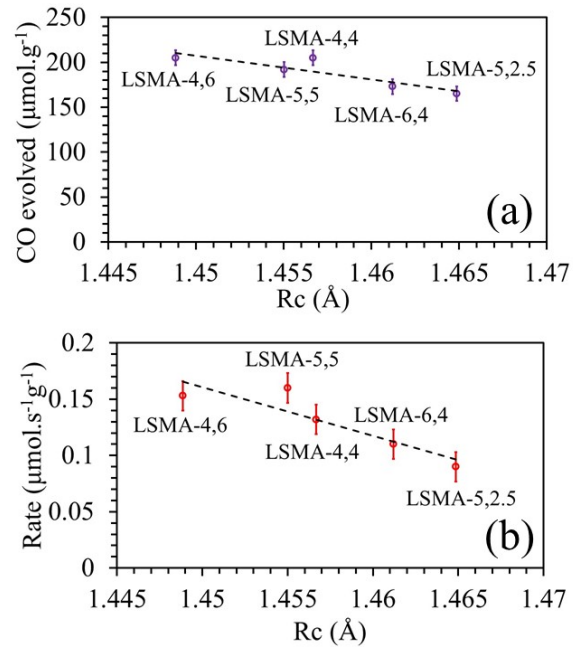


Figure S4. Amounts of CO evolved (a) and re-oxidation rates (b) as a function of critical radius for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

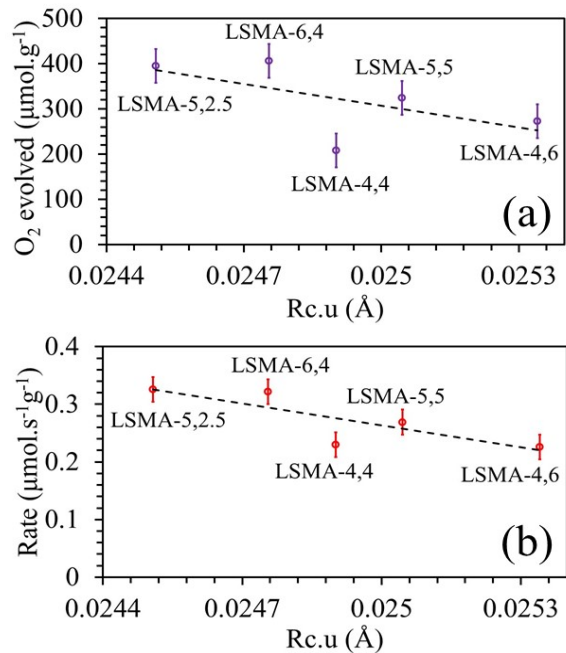


Figure S5. Amounts of O<sub>2</sub> evolved (a) and reduction rates (b) as a function of critical radius per unit cell volume for a series of La<sub>x</sub>Sr<sub>1-x</sub>Mn<sub>y</sub>Al<sub>1-y</sub>O<sub>3</sub> oxygen carriers.

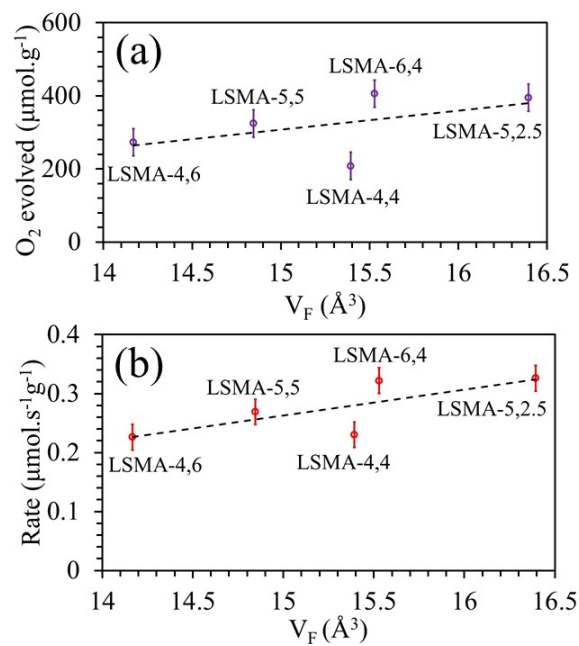


Figure S6. Amounts of  $O_2$  evolved (a) and reduction rates (b) as a function of lattice free volumes for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

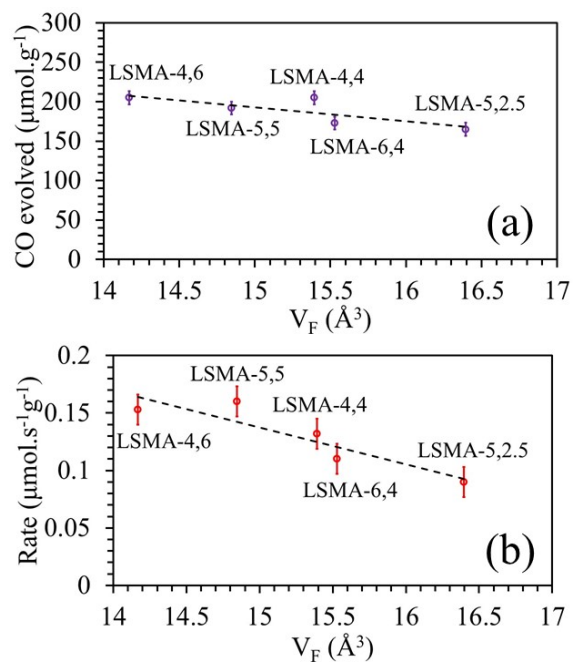


Figure S7. Amounts of CO evolved (a) and re-oxidation rates (b) as a function of lattice free volumes for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.



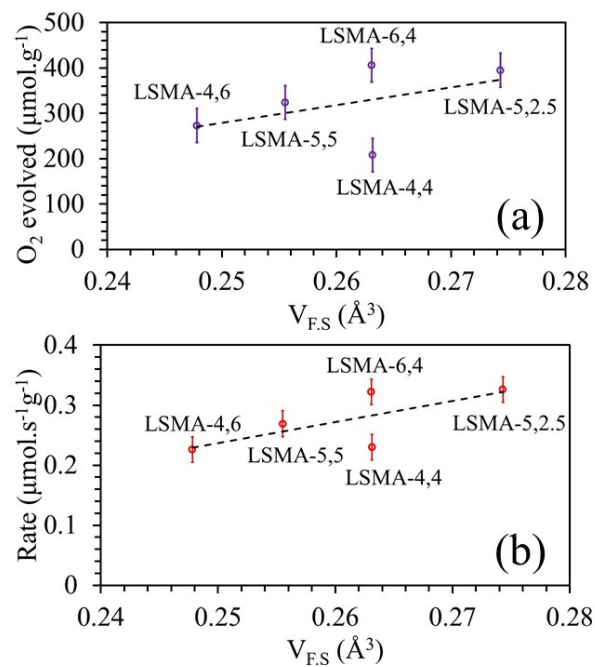


Figure S8. Amounts of  $O_2$  evolved (a) and reduction rates (b) as a function of specific free volumes for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

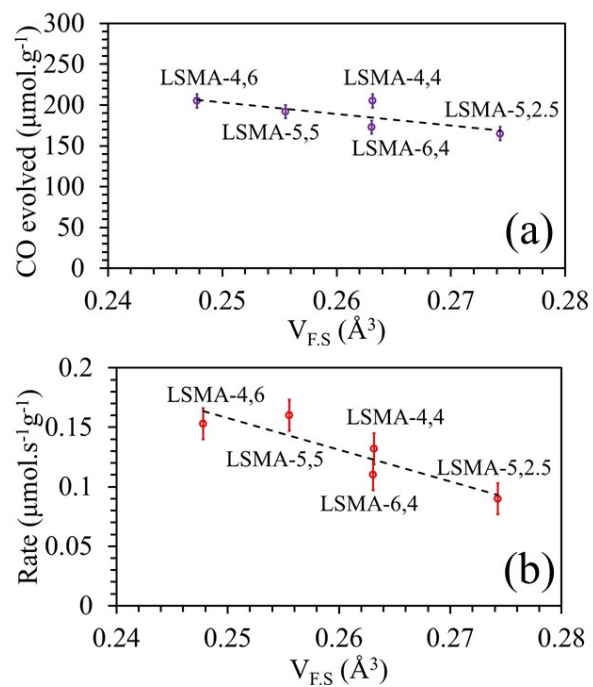


Figure S9. Amounts of CO evolved (a) and re-oxidation rates (b) as a function of specific free volumes for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

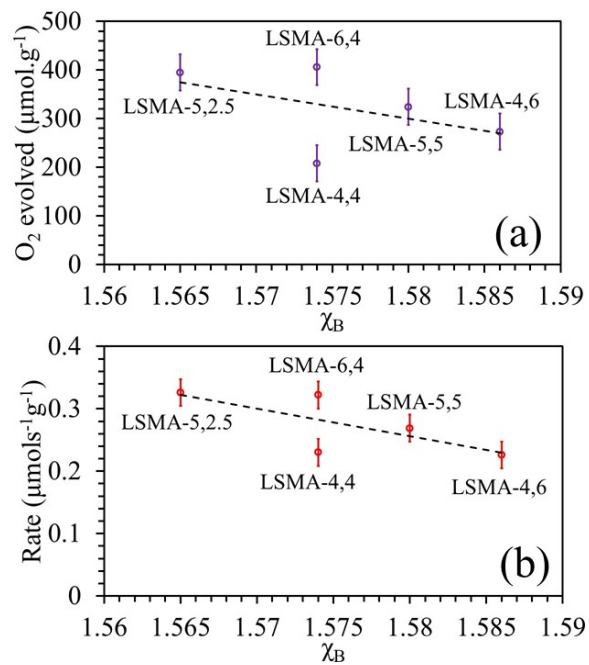


Figure S10. Amounts of  $\text{O}_2$  evolved (a) and reduction rates (b) as a function of B-site electronegativities for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

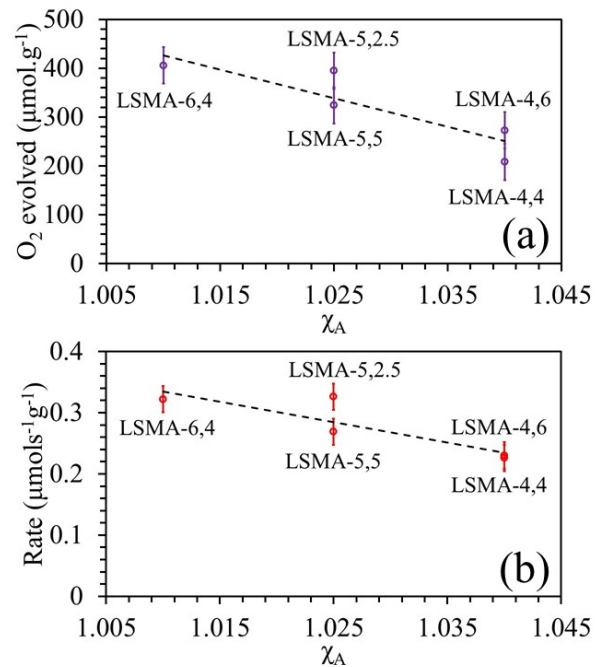


Figure S11. Amounts of  $\text{O}_2$  evolved (a) and reduction rates (b) as a function of A-site electronegativities for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

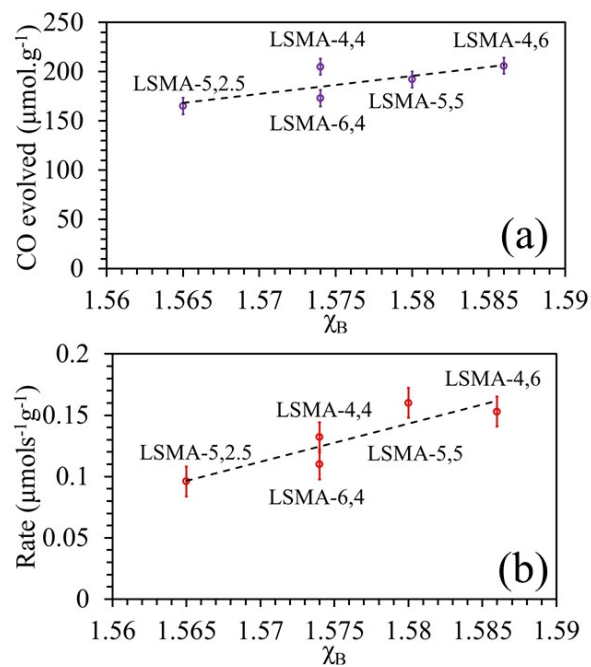


Figure S12. Amounts of CO evolved (a) and re-oxidation rates (b) as a function of B-site electronegativities for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

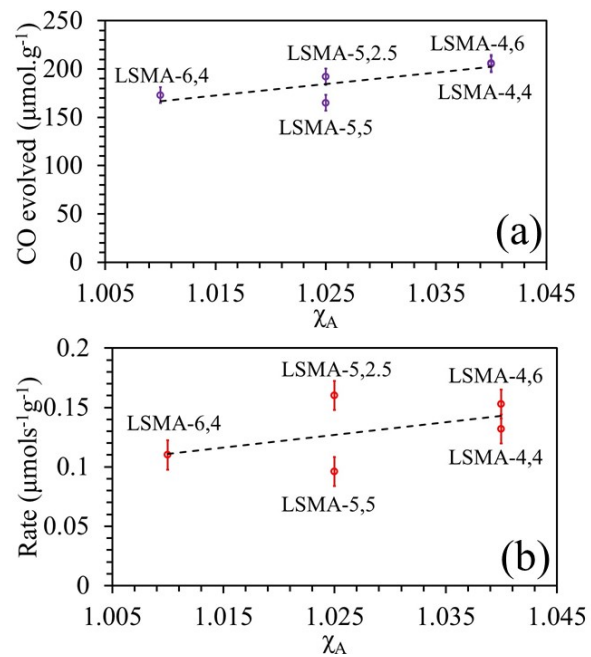


Figure S13. Amounts of CO evolved (a) and re-oxidation rates (b) as a function of A-site electronegativities for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

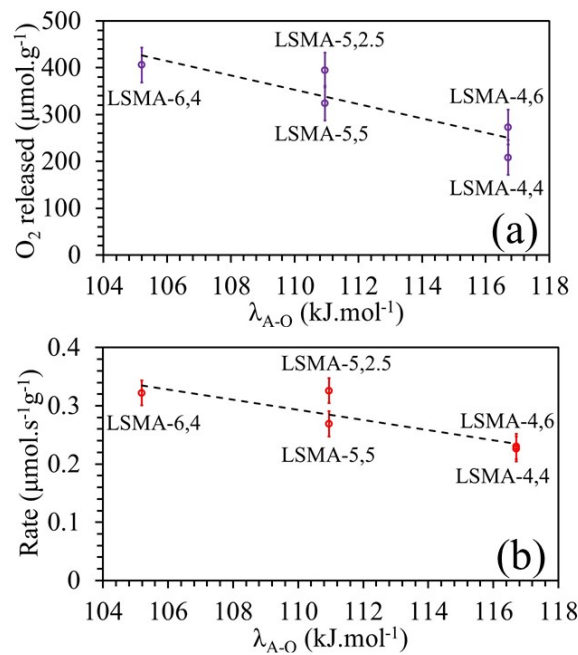


Figure S14. Amounts of  $\text{O}_2$  evolved (a) and reduction rates (b) as a function of A-O bond energies for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

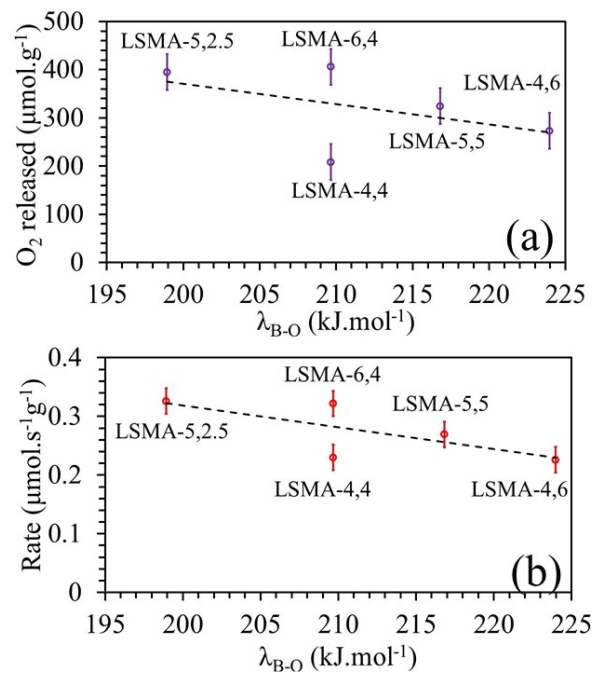


Figure S15. Amounts of O<sub>2</sub> evolved (a) and reduction rates (b) as a function of B-O bond energies for La<sub>x</sub>Sr<sub>1-x</sub>Mn<sub>y</sub>Al<sub>1-y</sub>O<sub>3</sub> oxygen carriers.



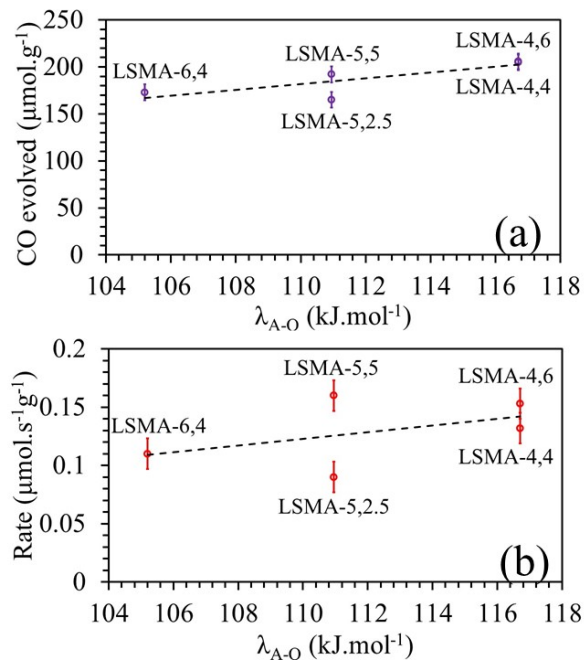


Figure S16. Amounts of CO evolved (a) and re-oxidation rates (b) as a function of A-O bond energies for a series of La<sub>x</sub>Sr<sub>1-x</sub>Mn<sub>y</sub>Al<sub>1-y</sub>O<sub>3</sub> oxygen carriers.

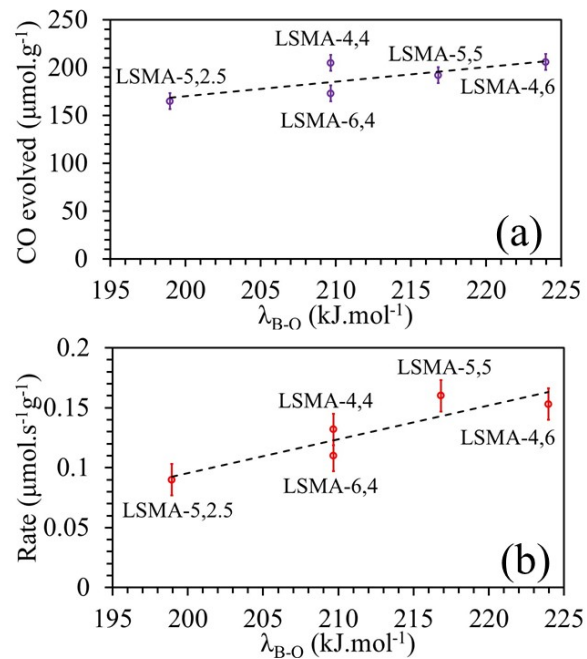


Figure S17. Amounts of CO evolved (a) and re-oxidation rates (b) as a function of B-O bond energies for a series of  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  oxygen carriers.

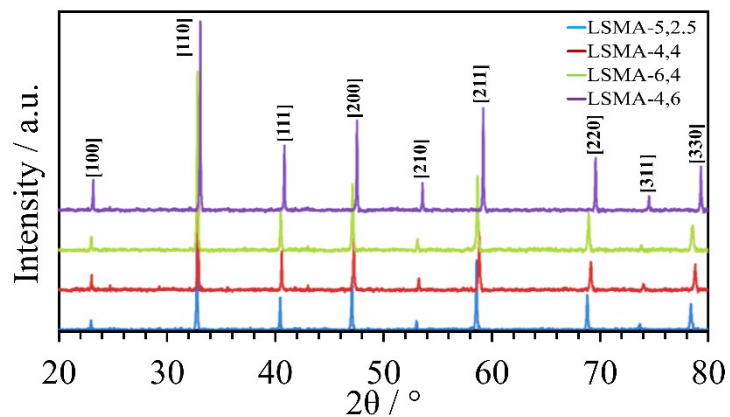


Figure S18. Wide angle powder XRD patterns observed for  $\text{La}_x\text{Sr}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$  series of perovskite oxygen carriers recovered after redox cycles comprising thermochemical reduction and subsequent  $\text{CO}_2$  splitting at  $1400^\circ\text{C}$  and  $1050^\circ\text{C}$  respectively.