

# Oxidizable Metals Improve Chemical and Electrochemical Stability on Perovskite Oxide Surfaces

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Segregation and phase separation of aliovalent dopants on perovskite oxide ( $ABO_3$ ) surfaces is detrimental to the performance of energy conversion systems such as solid oxide fuel/electrolysis cells and catalysts for thermochemical  $H_2O$  and  $CO_2$  splitting. One key reason behind the instability of perovskite oxide surfaces is the electrostatic attraction of the negatively charged A-site dopants (for example,  $Sr'_{La}$ ) by the positively charged oxygen vacancies ( $V_O^{\bullet\bullet}$ ) enriched at the surface. Here we show that reducing the surface  $V_O^{\bullet\bullet}$  concentration improves the oxygen surface exchange kinetics and stability significantly, albeit contrary to the well-established understanding that surface oxygen vacancies facilitate reactions with  $O_2$  molecules. We take  $La_{0.8}Sr_{0.2}CoO_3$  (LSC) as a model perovskite oxide, and modify its surface with additive cations that are more and less reducible than Co on the B-site of LSC. By using ambient pressure X-ray absorption and photoelectron spectroscopy, we proved that the dominant role of the less reducible cations is to suppress the enrichment and phase separation of Sr while reducing the concentration of  $V_O^{\bullet\bullet}$  and making the LSC more oxidized at its surface. Consequently, we found that these less reducible cations significantly improve stability, with up to 30x acceleration of the oxygen exchange kinetics after 54 hours in air at 550 °C achieved by Hf addition onto LSC. Finally, the results revealed a “volcano” relation between the oxygen exchange kinetics and the oxygen vacancy formation enthalpy of the binary oxides of the additive cations. This volcano relation highlights the existence of an optimum surface oxygen vacancy concentration that balances the gain in oxygen exchange kinetics and the chemical stability loss.