

DSL2023

HERAKLION, CRETE | GREECE

26 - 30 JUNE 2023

ABSTRACT:

Understanding the Effects of Acidic/Basic Binary Oxides on the Surface Exchange Kinetics of Mixed Conductors

D. Schwenkel¹, R. De Souza¹, G.F. Harrington^{1,2}

¹Institute of Physical Chemistry, RWTH Aachen University, Germany.

²Department of Chemistry, University of Bath, UK.

Given that the oxygen exchange reaction takes place on the outer surface, it is not surprising that modifying the surface composition of mixed ionic-electronic conductors (MIECs) leads to changes in the oxygen exchange rate. Intuitively, one might expect increases in the exchange rate to come from the addition of redox-active transition metal species, however, recently Nicollet et al. demonstrated that the surface exchange rate of $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_2$ (PCO) could be altered by more than 5 orders of magnitude by the infiltration of nominally inert, isovalent binary oxides. Even more surprising was that the enhancement/decrease in k is correlated with the acidity of the infiltrated species, with those more basic than PCO enhancing the surface exchange rate and those more acidic reducing it. Currently, however, a fully consistent mechanistic understanding of this effect is lacking.

This work aims to address two key questions: 1) Can this observed change in the surface exchange rate seen for PCO be extended to other MIEC systems? 2) Can we obtain a deeper insight into the underlying mechanism?

Here we demonstrate that the surface exchange rate of the perovskite $\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_{2.825+\delta}$ (STF) can be modified by over an order of magnitude, via the infiltration of CaO and SiO₂ species. As with the PCO system, changes in the exchange rate and conductivity of the samples correlate with the acidity of the infiltrated species, and no changes in the activation energies are observed, all suggesting that the same mechanism is responsible in both systems for the change in the oxygen exchange rate. Furthermore, using a combination of electrical conductivity relaxation (ECR) and oxygen isotope exchange annealing combined with depth profiling using secondary ion mass spectrometry (SIMS) in various atmospheres we provide a deeper insight into the underlying mechanisms.

[1] C. Nicollet, et al., Nat. Catal. 2020, 3, 913–920, DOI 10.1038/s41929-020-00520-x.