

**Developing fundamental understanding of oxygen exchange and associated expansion
in solid oxide fuel cell cathodes**

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In order to lower the cost of solid oxide fuel cells (SOFCs), both the low-temperature efficiency and long-term durability need to be improved. Fundamental studies of how fuel cell materials “breathe” oxygen under operating conditions can address these dual needs, since: 1) sluggish oxygen incorporation at the cathode dominates SOFC efficiency losses at low temperatures, and 2) chemical expansion during oxygen loss from the oxide can result in mechanical failure of the cell. In this work I investigate model cathode systems in order to understand what controls the oxygen exchange process and its related chemical expansion, with the goal of then being able to modify these processes to increase efficiency and durability.

To develop an understanding of the factors governing the cathode oxygen exchange rate, the relationship between electronic structure (particularly Fermi level) and oxygen exchange rate is pursued for the model system $\text{Sr}(\text{Ti,Fe})\text{O}_{3-x}$ (STF). Recent work¹ suggested that the rate-limiting step for oxygen exchange in STF is electron transfer from the cathode to adsorbed oxygen, implying that raising the Fermi level of the cathode would facilitate electron transfer and speed up oxygen exchange. Therefore, in this work the Fermi level is raised chemically by doping or electrochemically by atmosphere and/or applied voltage. To verify the desired changes in Fermi level, the electronic structure is derived *in situ* by thermodynamic defect chemical modeling of impedance and optical spectroscopy data. The resulting kinetics of oxygen exchange under cathode operating conditions are also probed using impedance spectroscopy and optical relaxation on thin films with well-defined geometries. Key results include the fabrication of high quality donor-doped STF thin film cathodes, the development of new optical techniques for determining the defect chemistry of the STF thin films, the demonstration of a successful rise in Fermi level by donor doping, and the observation of a decrease in activation energy of the cathode area-specific resistance with donor doping. Additionally, recent work on a similar model cathode system $[(\text{La,Sr})(\text{Ga,Ni})\text{O}_{3-x}]$, which demonstrates a reduced chemical expansion coefficient by controlling charge localization, will also be briefly discussed.

¹ W.C. Jung and H.L. Tuller, *Adv. Energy Mater.* 1 (2011) 1184