

First-Principles Insights into Oxygen Transport in Solid Oxide Fuel Cell Cathode Materials

Andrew M. Ritzmann,¹ Michele Pavone,² Ana B. Muñoz-García,² and Emily A. Carter³

¹Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544

²Department of Chemistry “P. Corradini”, University of Napoli Federico II, Napoli 80120, Italy

³Department of Mechanical and Aerospace Engineering, Program in Applied and Computational Mathematics, and Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544

Solid oxide fuel cells (SOFCs) generate electrical power cleanly and efficiently; however, sluggish cathode (oxygen reduction reaction, ORR) kinetics require high operating temperatures ($T_{op} > 800^\circ\text{C}$) [1] and impede wider deployment of this technology. Next-generation SOFC cathodes based on mixed oxygen-ion-electron conducting (MIEC) materials operate at intermediate-temperatures (IT, $600^\circ\text{C} < T_{op} < 800^\circ\text{C}$) because they allow bulk oxygen ion transport while retaining favorable electronic conductivity. [2] Bulk oxygen ion transport depends strongly on the oxygen vacancy concentration and the energy barrier for an oxygen ion to migrate into an adjacent vacant site. Using first-principles density functional theory (DFT) and DFT+U calculations, [3] we predict oxygen vacancy formation energies and migration barriers in several cathode materials. These provide insights which elucidate the relationships between cathode composition and oxygen transport and enable rational design of MIEC cathode materials.

Oxygen ion transport in perovskite-type (ABO_3) cathode materials depends on the material composition. We compare oxygen transport in $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ ($\text{M}=\text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$) to systematically analyze compositional effects. [4] Specifically, we study how Sr substitution alters the bulk structure, electronic properties, and oxygen vacancy formation energies of these materials. We also present oxygen migration pathways in LaCoO_3 and LaFeO_3 to understand the fundamental physics of the migration process. Our results provide insights for improving oxygen ion conductivities and guidelines for rationally designing new cathode materials.

Finally, we show how structure-property relationships in $\text{Sr}_2\text{Fe}_{1-x}\text{Mo}_x\text{O}_6$ (SFMO), a promising cathode material, [5] lead to high ionic and electronic conductivities. Our data explains the inherent non-stoichiometry of SFMO [6] and provides insight into the most favorable locations for oxygen vacancies. [7] We show that oxygen ion transport has a lower barrier in SFMO than in other MIEC cathodes, we explain the origins of this phenomenon, and we discuss how to optimize the Fe/Mo composition to obtain the best oxide ion conductivity.

References

- [1] Adler, S. B. *Chem. Rev.* 2004, 104, 4791–4844.
- [2] Lu, Z.; Hardy, J.; Templeton, J.; Stevenson, J. J. *Power Sources* 2012, 198, 90–94.
- [3] Mosey, N. J.; Liao, P.; Carter, E. A. *J. Chem. Phys.* 2008, 129, 014103.
- [4] Pavone, M.; Ritzmann, A. M.; Carter, E. A. *Energy Environ. Sci.* 2011, 4, 4933–4937.
- [5] Liu, Q.; Dong, X.; Xiao, G.; Zhao, F.; Chen, F. *Adv. Mater.*, 2010, 22, 5478
- [6] Muñoz-García, A. B.; Bugaris, D. E.; Pavone, M.; Hodges, J. P.; Huq, A.; Chen, F.; zur Loye, H.-C.; Carter, E. A. *J. Am. Chem. Soc.* 2012, 134, 6826–6833.
- [7] Muñoz-García, A. B.; Pavone, M.; Carter, E. A. *Chem. Mater.* 2011, 23, 4525–4536.