# A Novel Integrated Design for the Mixed Ionic-Electronic Conducting (MIEC) Perovskites

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Perovskites with excellent mixed ionic-electronic conductivity (MIEC) are the most promising candidate materials for the cathode of solid oxide fuel cells (SOFC) and oxygen transport membrane (OTM). Extensive investigations have been carried out on how to improve the electrical conductivities with adding doping elements and changing composition with the trial-and-error approach. However, the main challenge for the cathode material is: **The cathode candidate needs to meet the requirement on the chemical stabilities and electrical conductivities at the same time.** It is critical to the initial performance and more important to the long-term performance for SOFC and OTM. Even the most popular perovskites, like (La,Sr)MnO$_{3\pm\delta}$ (LSM) and (La,Sr)(Co,Fe)O$_{3\pm\delta}$ (LSCF), which have been investigated numerously, cannot satisfy the above two requirements.

Both the electrical conductivities and chemical stabilities of perovskites are affected by parameters, including temperature, gas species partial pressure, the stoichiometry of perovskites, and time. It is greatly needed to take one step back to understand the fundamentals and address the following two critical questions:

1) What is the mechanism determining the <u>electrical conductivities</u>?
2) What is the mechanism determining the <u>chemical stabilities</u> of perovskites?

Based on our recent exciting preliminary results on the application of computational thermodynamics in various fuel cell and membrane applications, we have successfully verified the hypothesis that the computational thermodynamics based on the CALPHAD approach is capable of investigating the electrical conductivities and chemical stabilities of perovskite candidates.



As shown above, the perovskite database developed with the CALPHAD approach is expanded to include Y, Zr, C, and H elements. The expanded thermodynamic database will provide the Gibbs energy description for individual phases, including perovskites, i.e. $G(T, p(O_2), x_i)$, as a function of temperature (T), oxygen partial pressure (p(O$_2$)), and composition ($x_i$). It is used to predict the chemical stabilities and the electrical conductivities of perovskites. Both of the predictions can be verified with the detailed experimental investigations. With the combined effort from the thermodynamic prediction and the experimental verification, perovskite candidates, which satisfy both the electrical conductivities and chemical stabilities requirements, can be recommended.

*The Novelty of The Project*: *The chemical stabilities and the electrical conductivities of perovskites can be predicted with the CALPHAD approach using* <u>*ONE single Gibbs energy description*</u>, *i.e. $G(T, p(O_2), x_i)$. Instead of only the regions with existing experimental data, the prediction will be applied to the experimentally unexplored or unachievable regions.*
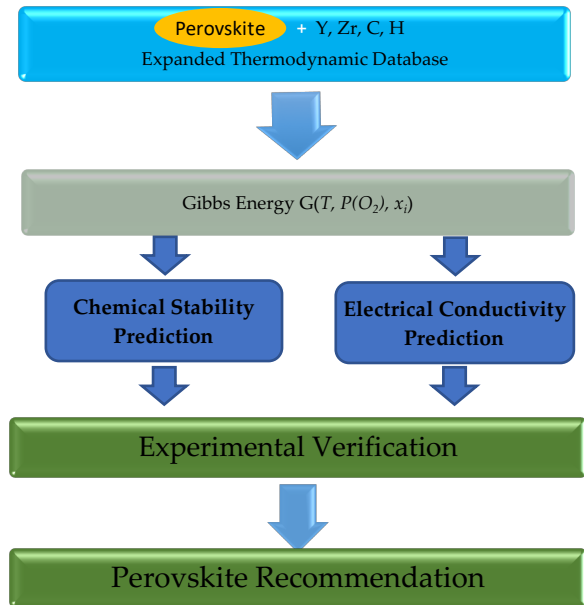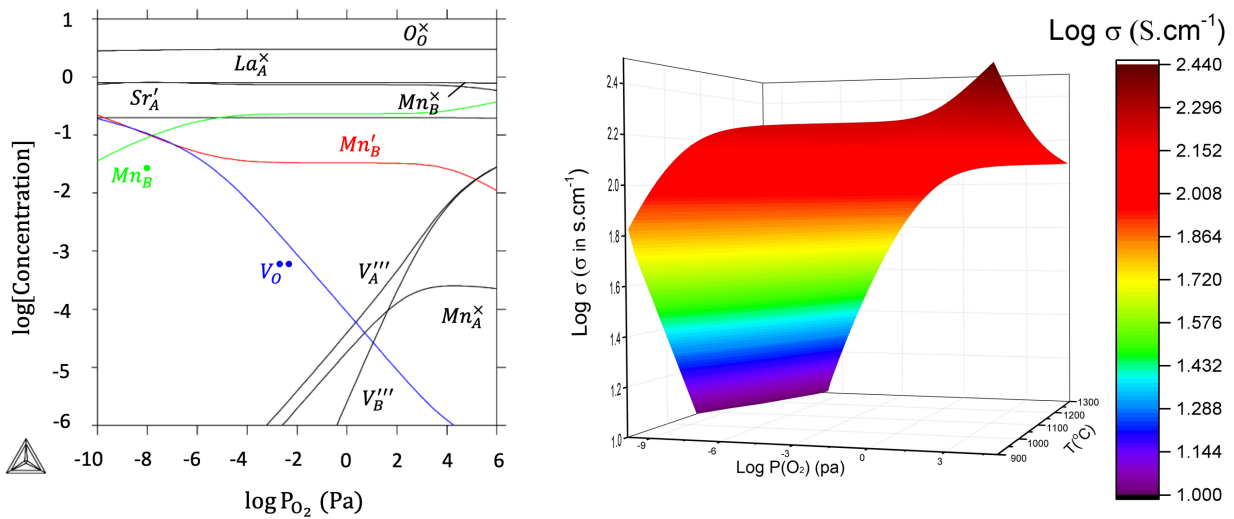
*The quantitative Brouwer diagrams of LSM20, the concentration of species at different p(O₂) at 1000ºC(left); 3-D contour of electronic conductivity as a function of p(O₂) and temperature (right).*

With this approach, recent success has been achieved by the PI in the electronic conductivity prediction for the p-type LSM, as shown above. Based on the quantitative Brouwer diagram for the carrier p ($[Mn_B^\bullet]$) in a wide p($O_2$) range, the electronic conductivity was recently predicted by the PI. Similar simulations have been carried out the predict the ionic conductivities. The MIEC perovskites can be predicted by considering these two conductivities at the same time. Meanwhile the chemical stabilities have been considered with electrolyte and also the impurities in gas. For example, LSCF-6428 and LSCF-7328 have been adopted to consider the formation of secondary phase $SrCO_3$ on the surface of LSCF; the threshold is defined as the moment $SrCO_3$ is forming. It clearly pointed out that there is a region in which LSCF is stable (**SrCoO₃ free region**) and the trend is that $SrCO_3$ prefers to form in a low temperature and high $CO_2$ partial pressure condition. It also shows the composition of LSCF has a significant impact on the chemical stabilities. With this type of simulations, we are able to design MIEC perovskite with the best chemical stabilities.
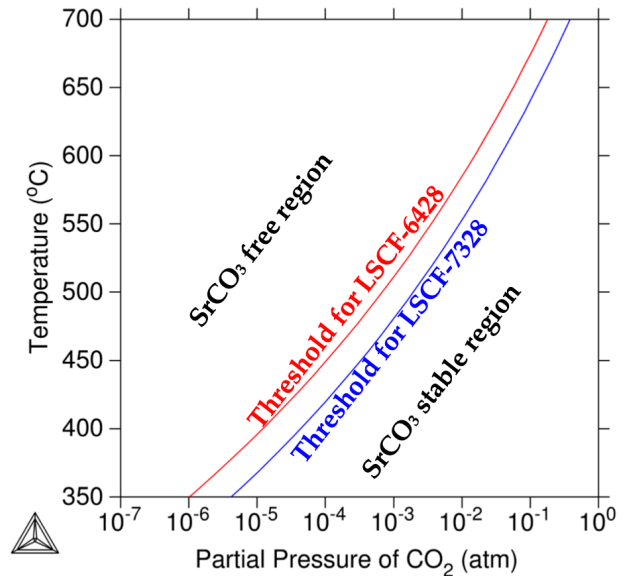


## Impact from the project

The results we achieved in this project plays critical role on securing two new DOE funding to continue the effort to design new perovskites. We have established wide collaborations with different groups from Boston University, University of Connecticut, Curtin University (Australia), Florida International University, and Praxair. Our results have attracted numerous interests and was invited for talks in TMS, MS&T, West Virginia University, Tsinghua University (China), Central South University (China), etc. Overall, 12 journal papers have been official published, and another 3 journal papers are accepted/in preparation. In addition, two graduate students have graduated and got their Ph.D. degrees and now work as Post-doc Fellows. Another graduate student is currently close to graduation and will defense his thesis in a year focusing on sub-topic of this project.