Theoretical Investigation of H₂ and CO Electro-Oxidation on the Sr:Fe₁₅Mo₆O₆₋₈ (001) Perovskite Surface under Anodic Solid Oxide Fuel Cell Conditions

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Introduction
Solid oxide fuel cells (SOFCs) are a promising electricity generation technology for distributed power generation due to its scalability, high fuel-to-electricity conversion efficiency and low pollutant emissions. Sr:Fe₃Mo₂O₆₋₈ (SFMO) perovskite has recently been proposed as a promising anode material for SOFCs. Despite the advantages of SFMO such as good ionic and electrical conductivity, its relatively low electro-oxidation activity is a major drawback which contributes to an overall low cell performance. It has been shown that adding a small amount of Ni to the anode improves the overall cell performance, but the presence of Ni decreases the sulfur tolerance of SFMO. Considering that understanding the fuel oxidation mechanism on perovskite surfaces such as SFMO is crucial for the development of alternative oxide based anode catalysts, we employed DFT+U methods and microkinetic modeling techniques to investigate the electrochemical oxidation of hydrogen and syngas fuels on the SFMO (001) surface under realistic fuel cell operating conditions. The role of Ni in improving the catalytic activity of SFMO and the sulfur poisoning mechanism of SFMO surface have also been examined.

Models and Methods
All calculations presented in this work were carried out using spin-polarized DFT+U theory with periodic boundary conditions as implemented in the VASP code. The calculations with PBE functional were carried out with a k-point mesh of 4×4×1 and a kinetic energy cutoff for the plane waves of 800 eV. The transition state structures were optimized using the climbing image-NEB and Dimer methods. The SFMO (001) slab has four SrO and four Fe(Mo)O₆ layers (Figure 1a) and the reaction mechanism was examined only on the Fe(Mo)O₆ terminated layer. To identify the rate determining steps, the DFT-derived parameters were employed in a microkinetic model to calculate the surface coverage of all adsorbed species and turnover frequency under realistic reaction conditions. The effect of anode bias potential was included by adding additional elementary steps in the model that allow the possibility of one- or two- electron charge transfer.

Results and Discussion
We employed constrained ab initio thermodynamic calculations to construct various surface models of SFMO under SOFC operating conditions. Three surface models with varying Mo concentration and oxygen vacancy content in the surface layer were identified which were then used to investigate the thermochromy and reaction barriers of the elementary steps involved in the H₂ and CO electro-oxidation mechanisms (Figure 1b). Simulated polarization curves reflect the kinetic activity of various SFMO surfaces and suggest that the SFMO surface with higher Mo concentration on the gas exposed layer is more active towards both H₂ and CO oxidation. When both H₂ and CO are present in the fuel stream (syngas) with some water, water gas shift (WGS, CO + H₂O → CO₂ + H₂) is rapid on these surfaces. Increasing the CO₂ concentration promotes the reverse WGS and decreases the electrochemical performance. Further analysis revealed that at relevant operating voltages and reaction conditions, water/CO₂ desorption is rate controlling for both H₂ and CO oxidation reactions and stabilizing the oxygen vacancy structure increases the overall rate. In addition, an increase in electrochemical activity and resistance towards sulfur poisoning is observed with increasing Mo content in the surface layer. However, according to our thermodynamic analysis, the surface Mo concentration tends to be very low under anodic SOFC conditions.

Finally, our calculations with small Ni particles on the SFMO surface suggest that the presence of Ni dramatically reduces the surface oxygen vacancy formation energy which could improve the overall electrochemical performance of the SOFC cell. However, the sulfur resistance will likely be reduced in the presence of Ni. These results suggest that increasing the Mo content in the gas exposed surface layer of SFMO will improve its overall electrochemical performance while maintaining excellent sulfur tolerance.

Significance
Understanding the fuel oxidation mechanism and identifying the rate limiting steps on the SFMO surface, an alternative anode material, has the potential to identify descriptors for the rational design of sulfur and carbon tolerant anode materials for solid oxide fuel cells.

Figure 1. (a) Model of Sr:Fe₁₅Mo₆O₆₋₈(SFMO) surface with 50% Mo on the top surface layer. (b) Proposed mechanism of H₂, CO oxidation and WGS reaction on the SFMO surface.

References