

# Combined Theoretical and Experimental Investigation and Design of H<sub>2</sub>S Tolerant Anode for Solid Oxide Fuel Cells

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## OBJECTIVE

Investigation and design of sulfur-tolerant anode electrocatalysts for solid oxide fuel cells.

## ACCOMPLISHMENTS TO DATE

This investigation is focused on understanding the interactions of various components present in coal syngas, such as H<sub>2</sub>S and CO, on the anode for Solid oxide fuel cell (SOFC). First a theoretical model is being developed to evaluate the impact of H<sub>2</sub>S on the anode material (Ni-YSZ). Second, the theoretical model will be verified by performing experiments. For the development of theoretical model, the structure of the electrolyte, Yttria stabilized Zirconia (YSZ), was optimized using Gaussian 03 software at b3pw91/1an12dz level of theory. Similarly, NiO was added to the electrolyte and optimized to simulate the SOFC anode, Nickel-Yttria stabilized Zirconia (Ni-YSZ).

After the structural optimization, the interaction of H<sub>2</sub> and H<sub>2</sub>S molecules with the anode (Ni-YSZ) was studied by quantum chemistry (QC) calculations using Gaussian 03. Calculated binding energy values for H<sub>2</sub> (-80 kcal/mol) and H<sub>2</sub>S (-21.4 kcal/mol) suggest that oxidation of both species are feasible but H<sub>2</sub> oxidation is more favorable than H<sub>2</sub>S at Ni-YSZ surface.

Interaction of the gas molecules was further investigated by extending the computational chemistry to Molecular dynamics (MD) calculations using Cerius<sup>2</sup> software. At 25° C, for H<sub>2</sub> and Ni-YSZ system, the radial distribution function (RDF) peak for Ni-H<sub>2</sub> pair was bigger than Zr-H<sub>2</sub>, Y-H<sub>2</sub>, and O-H<sub>2</sub> pairs, which denotes H<sub>2</sub> prefers to oxidize at Ni sites on the anode surface. On increasing the temperature from 25° to 600° and 850° C, the RDF peak for Ni-H<sub>2</sub> increased in contrast to same peak height for other pairs suggests that H<sub>2</sub> oxidation was enhanced with increasing temperature.

When H<sub>2</sub>S was included along with H<sub>2</sub> in the gas mixture, the RDF peak for Ni-H<sub>2</sub> pair was closer to surface than Ni-S pair at 850° C, which means H<sub>2</sub> has more affinity to the anode surface than H<sub>2</sub>S. Diffusion coefficient for H<sub>2</sub> molecules (absence of H<sub>2</sub>S) was calculated to be 10<sup>-7</sup>, 10<sup>-6</sup>, and 1.35 x 10<sup>-4</sup> cm<sup>2</sup>/sec at 25°, 600°, and 850° C respectively. But with the presence of H<sub>2</sub>S molecules, H<sub>2</sub> diffusivity was lowered by almost 20% to 1.10 x 10<sup>-4</sup> cm<sup>2</sup>/sec at 850° C.

A new component, carbon monoxide (CO) was included in the system along with H<sub>2</sub> and H<sub>2</sub>S. After optimization, its binding energy was -23.9 kcal/mol, suggesting CO oxidation is more favorable than H<sub>2</sub>S but is less favorable than H<sub>2</sub>. The diffusion coefficient for H<sub>2</sub> in the presence of CO molecules (850° C) was found to be 5 x 10<sup>-6</sup> cm<sup>2</sup>/sec, which is 96% lower than the diffusivity of H<sub>2</sub> without the presence of

CO molecules. These results show that mobility of H<sub>2</sub> molecules can be reduced with the presence of H<sub>2</sub>S and CO molecules in the gas mixtures.

#### **FUTURE WORK**

- Various composition of CO along with H<sub>2</sub>S will be investigated using QC and MD models to understand the H<sub>2</sub> oxidation at the anode surface of SOFC.
- A few more gas components (nitrogen and moisture) will also be included to the existing molecular models so as to increase the complexity of the system and predict the outcome for the experimental conditions.
- Design and construction of an experimental set up for solid oxide fuel cell so as to verify the models developed based on the first principles.

#### **LIST OF PAPER PUBLISHED**

A. Marquez, Y. De Abreu, and G. G. Botte, *Theoretical Investigation of NiYSZ in the Presence of H<sub>2</sub>S*, *Electrochemical and Solid-State Letters*, 9 (3) A163-A166 (2006).

#### **U.S. PATENT/PATENT APPLICATION(S)**

None at this time.

#### **CONFERENCE PRESENTATIONS**

2005 AIChE Annual Meeting: A. Marquez, Y. De Abreu, and G. G. Botte, “*Theoretical Investigations of Solid Oxide Fuel Cell anode Materials*”, October 30<sup>th</sup> – November 4<sup>th</sup>, 2005, Cincinnati, OH.

31<sup>th</sup> International Coal Conference, May 2006: A. Marquez and G. G. Botte, “*Theoretical Investigations of Solid Oxide Fuel Cell anode Materials in the Presence of H<sub>2</sub>/H<sub>2</sub>S/CO*”, The 31<sup>th</sup> International Technical Conference on Coal Utilization and Fuel Systems, May 2006, Clearwater, FL.

#### **AWARDS RECEIVED AS A RESULT OF SUPPORTED RESEARCH**

None at this time.

#### **STUDENTS SUPPORTED UNDER THIS GRANT**

Damilola Daramola (MS, Chemical Engineering, Ohio University)

#### **LIST OF PUBLISHED JOURNAL ARTICLE**

A. Marquez, Y. De Abreu, and G. G. Botte, *Theoretical Investigation of NiYSZ in the Presence of H<sub>2</sub>S*, *Electrochemical and Solid-State Letters*, 9 (3) A163-A166 (2006).

## **COMPLETED PRESENTATION**

2005 AIChE Annual Meeting: A. Marquez, Y. De Abreu, and G. G. Botte, “*Theoretical Investigations of Solid Oxide Fuel Cell anode Materials*”, October 30<sup>th</sup> – November 4<sup>th</sup>, 2005, Cincinnati, OH.

## **JOURNAL ARTICLES (SUBMITTED AND IN PREPARATION)**

A. Marquez and G. G. Botte, *Theoretical Investigation of NiYSZ in the Presence of CO, H<sub>2</sub>, and H<sub>2</sub>S*, under preparations (to be submitted to *Electrochemical and Solid-State Letters* in April 2006).

## **FORTHCOMING PRESENTATIONS**

31<sup>th</sup> International Coal Conference, May 2006: A. Marquez and G. G. Botte, “*Theoretical Investigations of Solid Oxide Fuel Cell anode Materials in the Presence of H<sub>2</sub>/H<sub>2</sub>S/CO*”, The 31<sup>th</sup> International Technical Conference on Coal Utilization and Fuel Systems, May 2006, Clearwater, FL.

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