

Combined Theoretical and Experimental Investigation and Design of H₂S Tolerant Anode for Solid Oxide Fuel Cells

Gerardine G. Botte
Ohio University
183 Stocker Center
Athens, OH 45701
Phone: 740-593-9670
Fax: 740-593-0873
Email: botte@ohio.edu

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OBJECTIVE

Investigate the mechanism for deterioration of Solid oxide fuel cell anode (Ni-YSZ) by H₂S present in coal syngas, using molecular modeling and validating the theoretical model with experimental data.

ACCOMPLISHMENTS TO DATE

The study is focused on understanding the interactions of H₂S and CO molecules, present in coal syngas, with anode material of solid oxide fuel cells (SOFC). The investigation involves use of molecular modeling (Quantum Chemistry and Molecular Dynamics) of the anode material (Ni-YSZ) with gas molecules (H₂, H₂S and CO) to predict a theoretical model for oxidation of H₂ in SOFC. In this performance period, we extended the theoretical study to combinations of gas molecules so as to bring the gas composition closer to coal syngas. QC calculations for Anode+H₂+H₂S, Anode+H₂+CO and Anode+H₂S+CO systems resulted in -21.6, -155.5 and -134.6 kcal/mol of binding energies respectively. The binding energy for Anode+H₂+H₂S system is more than pure H₂ (-80.1 kcal/mol) because H₂S hinders the oxidation of H₂ on Ni-YSZ surface. But on the contrary, the addition of CO molecule to either H₂ or H₂S has resulted in lesser binding energy than the pure H₂ or pure H₂S (-21.4 kcal/mol). These binding energies suggest that addition of CO gas molecule can help in oxidation of both H₂ and H₂S gases. The presence of CO in gas mixture will result in coking of the anode, which can be prevented by addition of moisture to the gas mixture. Binding energies for the Anode systems having moistures are H₂O: -36.9 kcal/mol, H₂O+H₂: -37.1 kcal/mol, H₂O+H₂S: -46.4 kcal/mol and H₂O+CO: -31.6 kcal/mol. These binding energies indicate that addition of moisture makes the above systems very similar. In all our QC calculations using Gaussian 03, we have calculated the Raman spectra for each system so that we use this information for experimental verification.

Molecular dynamics calculations provide the diffusion coefficient of the gas molecules to help in understanding the QC results. Diffusion coefficient of H₂ was lowered to 5×10^{-6} cm²/s from 1.35×10^{-4} cm²/s with the addition of 2% CO gas molecules which means oxidation of H₂ is slowed by the presence of CO. In a system of 2% H₂S, 2% CO and the rest H₂, the diffusivity of H₂ is lowered to 9×10^{-6} cm²/s and H₂S diffusivity is 2×10^{-9} cm²/s as compared to 1×10^{-5} cm²/s in H₂+H₂S(2%) system. Binding energies for moisture based systems were very close and MD calculation of H₂+H₂O(1%)+CO(1%) system shows very high diffusion coefficient for H₂O, 8×10^{-3} cm²/s, and H₂ diffusivity has been lowered to 4.9×10^{-7} cm²/s from 1.35×10^{-4} cm²/s for pure H₂ system. Even though moisture is required to avoid coking of SOFC anodes and electrolyte from CO, but it also slows the diffusion of other gas molecules to anode surface.

Finally to verify the theoretical models, experimental data are required. We have been working on the design and construction of an experimental setup far different from conventional SOFC testing system. A compact two quartz tubes have been constructed to hold the SOFC cells. These quartz tubes will be placed inside a furnace, which is made of three small furnaces, to maintain a temperature of 850° C. Anode (Ni-YSZ) side of the cell will have Pt reference electrode for measuring anode voltage and Pt is also used as cathode, which will be exposed to air. Since these experiments involve H₂S gas, we are undertaking rigorous measures on personnel safety. We are very close to begin performing experiments using the setup.

FUTURE WORK

- QC and MD calculations of all the gas components (H₂, H₂S, CO) together with and without moisture.
- Nitrogen will be added to the existing systems for molecular modeling so as to verify with experimental data. Nitrogen is the dilution gas used along with H₂ in experimental setup.
- Perform experiments and verify the models 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 H₂S*, *Electrochemical and Solid-State Letters*, 9 (3) A163-A166 (2006).

U.S. PATENT/PATENT APPLICATION(S)

None at this time.

CONFERENCE PRESENTATIONS

D. Daramola, M. Muthuvel, A. Marquez and G. G. Botte, “*Theoretical Investigation of Solid Oxide Fuel Cell Anode Materials in the presence of H₂, H₂S and CO*”, National Society for Black Engineers (NSBE) National Conference, March 28th – April 1st 2007, Columbus, OH.

A. Marquez and G. G. Botte, “*Theoretical Investigations of Solid Oxide Fuel Cell anode Materials in the Presence of H₂/H₂S/CO*”, The 31st International Technical Conference on Coal Utilization and Fuel Systems, The Clearwater Coal Conference, May21-25, 2006, Clearwater, FL.

AWARDS RECEIVED AS A RESULT OF SUPPORTED RESEARCH

- Damilola Daramola has been named a 2007 BCA Scholar by National Society for Black Engineers (NSBE) for academic achievements.
- Damilola Daramola received Third prize for his poster in The Eastern Regional Chemical and Materials Engineering Graduate Symposium at University of Kentucky, Lexington, KY.

STUDENTS SUPPORTED UNDER THIS GRANT

Damilola Daramola (MS, Chemical Engineering, Ohio University)

LIST OF PUBLISHED JOURNAL ARTICLE

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COMPLETED PRESENTATION

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A. Marquez, Y. De Abreu, and G. G. Botte, “*Theoretical Investigations of Solid Oxide Fuel Cell anode Materials*”, American Institute for Chemical Engineers (AIChE) Annual Meeting, October 30th – November 4th, 2005, Cincinnati, OH.

JOURNAL ARTICLES (SUBMITTED AND IN PREPARATION)

A. Marquez and G. G. Botte, *Theoretical Investigation of NiYSZ in the Presence of CO, H₂, and H₂S*, under preparations (to be submitted to *Electrochemical and Solid-State Letters* in April 2007).

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