548c Theoretical Investigations of Solid Oxide Fuel Cell Anode Materials

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INTRODUCTION

Solid oxide fuel cells (SOFCs) are able to handle contaminants such as CO and CO_2 present in coal-derived syngas. However, coal-syngas also contains H_2S at high concentrations (between 0.5-5% H_2S depending on where the coal is mined)[1], being this contaminant one of the major obstacles to implementing a coal-syngas SOFC, since an anode catalyst able to handle the presence of H_2S without deterioration over time has not been developed.

In this subject, several attempts, based on inefficient traditional trial-and-error experimental methods, have been made in order to develop an anode material that can withstand the hydrogen sulfide presence in the fuel,[2-17] but it is still unclear the mechanisms involved in the degradation of the materials.

On the other hand, few attempts have been made to use molecular modeling to understand the structure of materials for SOFC applications, while no attempts have been made to use this technique to aid in the development of H_2S tolerant electrodes for SOFC applications. Some researchers[18-33] have used computational chemistry methods to study several properties of the electrolyte material YSZ as well as Zirconia. The objective of this paper is to investigate the interactions of H_2 and H_2S with a commercially available anode material for SOFCs in order to provide a better understanding of the degradation of the material in the presence of H_2S. The aid of this paper is on the development of sulfur tolerant anodes.

METHODOLOGY

Ni-YSZ was the selected basis material to be studied, because it is one of the commercial anode materials currently available for solid oxide fuel cells. The chemical interactions and the reactivity of H_2S and H_2 with the selected electrode material (Ni-YSZ) were determined by using first principles modeling (ab initio). Gaussian 03 [34,35] was used for all the quantum chemistry (QC) calculations, at the b3pw91/lanl2dz level of theory. [34-36]

Molecular dynamics (MD) simulations[37,38] were performed to: determine diffusion coefficients, identify structural variations at each phase, and determine packing and orientation of the chemical species at the surface of the electrode material. The software Cerius2, with the Universal Force Field (UFF), [39] was used for the MD studies.

RESULTS AND DISCUSSION

A unit cell structure of YSZ was optimized, by adding Yttrium to the ZrO2 (Figure 1).

Figure 1. Optimized electrolyte YZrO (5Zr-1Y-12O)

When Nickel oxide (NiO) was added to YZrO (simulating the anode material NiO-YSZ), a large binding energy value of -130 Kcal/mol showed that the electrode structure is very stable. This suggests that the NiO-YZrO system can reasonably represent the anode material.

Interactions of H_2 and H_2S with the optimized Ni-YZrO: For the hydrogen case a binding energy of -80.1 Kcal/mol was found while for the H_2S case the binding energy was -21.4 Kcal/mol. This finding suggests that the oxidation of H_2 is thermodynamically preferred at the anode. However, the oxidation of H_2S is also thermodynamically feasible.

From the Molecular Dynamics[37-38] (MD) studies, the radial distribution function (RDF) of the different components of the anode material (Ni, Zr, Y, O) was calculated when hydrogen is present in the environment at low temperature (25 °C). The maximum RDF is denoted by the pair Ni-H. These data indicate that hydrogen prefers to be sited adjacent to Ni ions which will favor the H_2 oxidation on the Ni sites.

On the other hand, when the temperature is increased to 600 and 850 °C, similar results in the RDF and atoms distances were obtained for the pairs Zr-H, Y-H and O-H, except for the pair Ni-H, for which the height of these peaks increases with increasing the temperature. This indicates that the oxidation of H_2 is enhanced by increasing temperature, that is diffusion limitations are minimized.

From the MD simulations in an H_2S/H_2 environment at 850 °C, we found that the RDF Ni-H peak is smaller than the one without H_2S and is closer than the Ni-S pair case, indicating that the H_2S is less attracted to the surface than hydrogen and the hydrogen moves slower in the presence of H_2S, in agreement with the QC results. This also suggests that the H_2S oxidation could start taking place but at a slower rate than H_2 oxidation (mass transport limitations are important).

Diffusivities: the diffusion coefficients of H_2 in gas phase close to the surface of the electrode were found to increase when increasing temperature, where values in the order of 10^{-7} cm^2/s, 10^{-6} cm^2/s, and $1.35x10^{-4}$ cm^2/s for 25 °C, 600 °C and 850 °C, respectively were found. When H_2S is present in the mixture, the diffusivity of hydrogen was about $1.10x10^{-4}$ cm^2/s at 850 C (20% lower than for H_2 alone). Also, the diffusion coefficient of H_2S ($1x10^{-5}$ cm^2/s; 850 °C) is always lower than the one for H_2. Moreover, in agreement with the RDF results, it is clear that the H_2S molecules tend to be surrounded by H_2 molecules, which as it has been said before slows the hydrogen oxidation.

CONCLUSIONS We can conclude that the Quantum Chemistry and Molecular Dynamics can provide information that is useful to determine favorable materials for the anode electrode and its stability in the oxidation medium, and that these techniques reproduce with great certainty the experimental findings.

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