First principles studies of electrochemical reactions at solid oxide fuel cell (SOFC) anodes

David Ingram and Suljo Linic*
University of Michigan, Ann Arbor, MI, 48109
*linic@umich.edu

Introduction

Solid oxide fuel cells (SOFC) are high temperature electrochemical systems that convert the chemical energy of combustible fuels into electrical energy. The higher efficiency achievable in this energy conversion process, in contrast to conventional energy conversion methods, makes SOFCs a promising energy conversion device.

While SOFCs are well-established electrochemical devices, it is surprising how little is known about electrochemical reactions that take place at electrode/electrolyte interface and to a large extent govern the performance of SOFCs. These reactions are difficult to probe since they take place in presence of strong electric fields and at the electrode/electrolyte interface, which is inaccessible and difficult to probe with conventional spectroscopic experimental techniques.

We have employed quantum Density Functional Theory (DFT) calculations to study the elementary step mechanisms of electrochemical oxidation reactions over SOFC anodes.[1,2] We illustrate that the first principles tools can provide meaningful guidelines towards identifying the electrochemical elementary steps that control the current and contribute to anodic overpotential losses.

Materials and Methods

We performed the DFT calculations with the Dacapo pseudo-potentials plane wave code [www.fysik.dtu.dk/CAMPOS]. The density of valence electrons was determined self-consistently by iterative diagonalization of Kohn-Sham Hamiltonians. The plane wave basis set used to describe the one-electron states was cut off at 350 eV. An electronic temperature ($k_b T$) of 0.1 was used during calculations with the final results extrapolated to 0 K. The forces were minimized to 0.05eV/A.

DFT calculations are used to calculate electronic energies of various reaction intermediates on electrode surface. The energies obtained from DFT calculations are then suitably corrected for the effect of temperature and pressure. We also account for the effect of potential bias and electric field, which are present under SOFC operating conditions. While we focus on anode reaction, similar approach could be used to analyze any electrochemical reaction.

Results and Discussion

The overall reaction for the electro-chemical oxidation of H_2 over an SOFC anode can be written as:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$
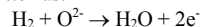
Various mechanisms for the above reaction have been postulated. For example, is has been proposed that hydrogen molecule from gas phase dissociates over two vacant sites on metal. Oxygen anions from the electrolyte are transferred onto the metal forming adsorbed oxygen and also transferring two electrons to the metal anode. The adsorbed hydrogen reacts with adsorbed oxygen to form adsorbed OH* on the metal. In the final step adsorbed OH* and H* undergo a surface reaction to form water which desorbs into gas-phase. We have utilized DFT calculations to study various electro-chemical elementary steps on multiple facets of various metals.

In Figure 1(a) we show the DFT-calculated free energies associated with various elementary steps for electrochemical oxidation of hydrogen on four different metals (No, Ni, Co, Cu) at operating potential of 0.8 V (with respect to standard oxygen electrode) and T =1073 K. We also show in Figure 1(b) the volcano plot where normalized electrochemical activity for various metals was calculated, by combining first principles calculations and micro-kinetic modeling, as a function of oxygen binding energy. The activity predictions were confirmed in the experimental measurements of the I/V characteristics for various anode materials

We have obtained the following conclusion: (i) the adsorption energy of oxygen on an anode surface is an excellent descriptor of the electro-catalytic activity of different materials, (ii) optimal anode electro-catalysts, aside for the stability requirements, need to be able to activate hydrogen (or hydrocarbon) and adsorb oxygen within an adsorption energy window which allows for a facile transfer of oxygen anions from an electrolyte to a metal, and an exothermic water desorption (metal-oxide formation needs to be prevented), (iii) the surface concentration of low-coordinated sites plays an important role.
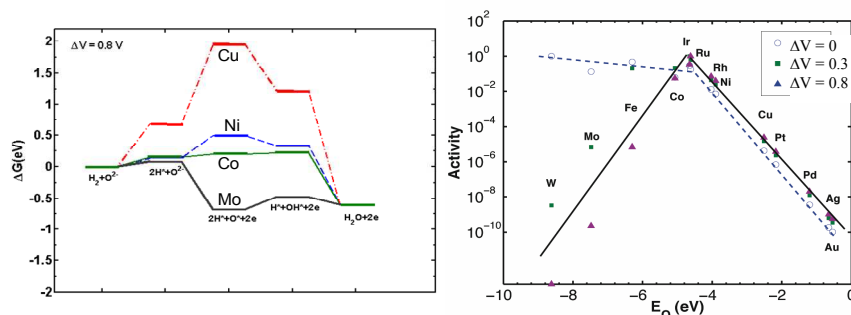

Figure 1. A) Free energies (at T=1000 K, P(H_2)=1 atm, P(H_2O) = 0.05 atm) for various elementary steps associated with electrochemical hydrogen oxidation, B) Normalized activity of various metal electro-catalysts. The activity is obtained with the parameters calculated in the first-principles calculations.

Significance

Understanding of elementary step mechanisms of electrochemical reactions is crucial for the identification of those steps that are the major contributors to overpotetnial losses. These insights are critical for more systematic approach towards the discovery of novel electro-catalysts will improved performance.

References

1. Joydeep Mukherjee, Suljo Linic, submitted to Journal of Electrochemical Society.
2. E.Nikolla, A. Holewinski, J. Schwank, S. Linic;, JACS, 2006; *128*(35); 11354-11355.