# First-principles Design of Electrocatalysts for Direct Borohydride Oxidation

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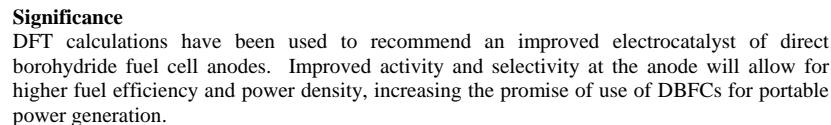
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## Introduction

Direct Borohydride Fuel Cells (DBFCs) have the potential to generate high power densities for use in portable power applications. Current applications are limited, in part, by the lack of an effective anode electrocatalyst. Though a number of pure metals have been tested as anodes, no previously tested electrocatalyst demonstrates both the required activity and selectivity [1]. Overpotentials on Au anodes, a selective catalyst, limit the overall cell efficiency to low values and little is known of the elementary electrocatalytic mechanisms. Platinum demonstrates a sizable current at lower overpotentials, but non-selective hydrolysis reactions compete with direct oxidation. Difficulties associated with experimental characterization of elementary kinetics for the 8 electron reaction motivate our application of density functional theory (DFT) methods. DFT calculations examine the mechanism of borohydride electro-oxidation over Au(111) and Pt(111) surfaces. Stable surface intermediates and limiting steps are identified. Key energetic parameters are identified and evaluated for pure and bimetallic electrocatalysts. Au-Cu alloys are determined from DFT calculations to be encouraging for improved performance, and initial experimental testing will be discussed.

## Computational Methods

Calculations were performed using the ab-initio total-energy and molecular-dynamics Vienna ab-initio simulation program (VASP). Two approaches were used to represent the electrochemical nature of the catalytic interface. The first, [2] uses a metal-vacuum slab interface to determine the interaction of individual species with the electrode surface. The energy of ion or electron species produced or consumed in individual reaction steps is dictated by their energy in the bulk electrolyte or by the electrode potential. Extensions of this approach to approximate the potential dependence of elementary step activation barriers will also be discussed. A second method, the double-reference method developed by Neurock and co-workers, includes solvation and electric field variation [3-4].

## Results and Discussion

The potential dependent energetics of borohydride adsorption and elementary oxidation steps were determined over Au(111) and Pt(111) surfaces. Oxidative adsorption of $BH_4^-$ is weak and molecular to the Au(111) surface whereas adsorption to Pt(111) is dissociative and highly exothermic at low overpotentials. Weak adsorption on Au catalysts, producing a low coverage of reactive surface species, partially explains their low activity. Strong dissociative adsorption on Pt(111) produces a high surface coverage of hydrogen, and molecular hydrogen evolution competes with oxidation processes. An optimal catalyst must therefore prefer molecular adsorption, with stronger adsorption than on the Au(111) surface.

DFT calculations were used to evaluate the elementary reaction energetics for surface oxidation steps. The ability to adsorb OH* species and break O-H bonds limits the rate of oxidation over Au(111) and Pt(111) surfaces. Specifically, dissociation of O-H bonds in

$B(OH)_2^*$ and BOOH* intermediates limits the formation of the $BO_2^-$ product over both Au(111) and Pt(111) surfaces. An optimal catalyst must show greater activity for these reaction steps to increase the overall rate of borohydride electro-oxidation.

The energetics of oxidative borohydride adsorption and O-H dissociation of BOOH* were calculated over a series of late transition metals. The Cu(111) surface shows stronger molecular adsorption [-0.44 eV adsorption energy at -0.5 V-SHE vs. +0.43 eV over Au(111)] as well as a more exothermic O-H bond breaking reaction energy for BOOH* (-0.52 eV at -0.5 V-SHE over Cu(111) versus +0.24 eV and +0.46 eV over Au(111) and Pt(111) surfaces). Copper electrodes, however, are likely to oxidize at potentials of interest for application as DBFC anodes. Cu-Au alloys, however, are stable under these conditions. All oxidation steps are favorable over $Au_2Cu_1(111)$ [Figure 1] at -0.45 V-SHE, 25 mV lower than over the Au(111) surface. Cu-Au bimetallics are therefore proposed as improved anode electrocatalysts for DBFCs. Initial experimental testing, planned for Spring 09, will be discussed.



**Figure 1.** Reaction energy diagram for $BH_4^-_{aq}$ oxidation over the $Au_2Cu_1(111)$ surface.

## Significance

DFT calculations have been used to recommend an improved electrocatalyst of direct borohydride fuel cell anodes. Improved activity and selectivity at the anode will allow for higher fuel efficiency and power density, increasing the promise of use of DBFCs for portable power generation.

## References

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