Reactivity Descriptors for Improving Direct Methanol Fuel Cell Anode Catalysis

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Introduction

Direct methanol fuel cells (DMFCs) show promise as energy conversion devices for multiple applications. [1] However, several technical challenges, such as the high overpotential associated with the anode reaction, limit the efficiency of DMFCs. To improve the efficiency of DMFC anodes, bi- and tri-metallic catalysts are employed, generally based on Pt-Ru. However, the cost of these materials is prohibitive. Thus there is interest in finding new anode catalysts that (1) have high efficiency and (2) are less expensive than current state-of-the-art.

Materials and Methods

In this work, we use periodic, self-consistent Density Functional Theory (PW91-GGA) to calculate key aspects of the electrochemical potential energy surface for the anode reaction on the close-packed surface of 12 transition metals. Entropy calculations are performed so as to calculate the reaction free energies associated with the methanol decomposition reaction. In addition to the evaluation of free energies on the close-packed surface, a similar analysis is performed on the (100) surface of 8 face-centered cubic transition metals. The standard hydrogen electrode reference, as described in reference 2 is utilized to include the effect of electrochemical potential on the methanol oxidation reaction.

Results and Discussion

We evaluate different reaction pathways for methanol electrooxidation and the associated 'onset potential' (i.e., the potential at which there exists a reaction pathway where all reaction steps have negative free energies) for each reaction on each transition metal surface studied. As the overpotential is a key variable in determing fuel cell efficiency, this allows us to evaluate the efficacy of each catalyst surface by comparing the overpotential necessary for the reaction to take place.
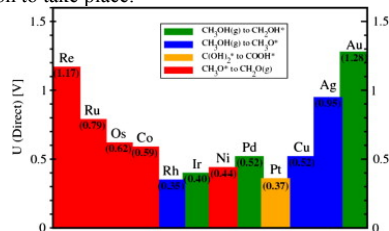

Figure 1. Onset potential for Methanol Electroxidation on 12 transition metals

In addition to the onset potential, this analysis provides us with two key pieces of information: the mechanistic pathway at low potentials and the potential-determining step (what is the most difficult thermodynamic step along the mechanistic pathway at low potentials). Figure 1 shows the onset potential and potential-determining step on the close-packed surface of the 12 transition metals studied.

By evaluating the onset potential of multiple facets of the same metal, one can also see what surfaces will dominate reactivity at low potentials; in addition, one can evaluate the change in reaction mechanism across facets of the same metal, thereby giving some information regarding the structure sensitivity of this reaction on that metal.

In addition to looking at the onset potential on monometallic alloys, this work can be extended to any surface by use of 'reactivity descriptors'. The free energy of all intermediates in methanol electroxidation can be linearly correlated to the free energy of only two surface species—CO* and OH*. Thus, by knowing only the free energy of these two intermediates, one can calculate the onset potential and potential-determining step on a generalized surface, as shown in figure 2.
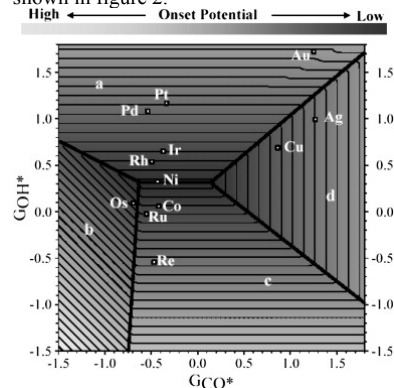

Figure 2. The potential-determining steps for the direct mechanism plotted with G_{CO}^* and G_{OH}^* as descriptors. The potential-determining steps for each region are as follows: (a) $H_2O \rightarrow OH$; (b) $CO + OH \rightarrow CO_2$; (c) $H_3CO \rightarrow H_2CO$; (d) $H_2CO \rightarrow CHO$. Iso-potential lines are also included for reference. Each line represents a difference of 0.1 V.

Significance

From this work we can predict the onset potential and reaction mechanism for the DMFC anode reaction on multiple transition metals surfaces. Using the framework of reactivity descriptors described herein, we can screen for alloy surfaces which may minimize the overpotential and therefore improve the DMFC efficiency.

References

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