

Reversible Potentials for Adsorbed Intermediates during Methanol and Formic Acid Electrooxidation on Platinum. Implications for Fuel Cells and Carbon Dioxide Reduction

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Introduction. The standard reversible potentials for 17 intermediates that could plausibly participate in the electro-oxidation of methanol and formic acid to carbon dioxide were calculated from reaction Gibbs energies obtained using density functional theory. They span a range of 5.5 V. When the intermediates are adsorbed on a platinum electrode, the reversible potentials shift due to the bonding stabilizations of the reactant and product of the one-electron reaction. Using internal energies rather than Gibbs energies of adsorption on Pt(111), in what this lab calls the linear Gibbs energy approximation, reversible potentials for several pathways for methanol and formic acid oxidation were determined. Bonding to the platinum greatly reduced the range of reversible potentials as seen in solution to 1.4 V.

Methanol oxidation. The calculated standard reversible potential for methanol reduction to carbon dioxide was -0.095 V. When the intermediates are adsorbed, most electron transfer reaction steps with reversible potentials negative of -0.095 V will have small activation energies and those with reversible potentials greater than -0.095 V will have high activation energies. Using this selection criterion, the favored among several routes is $\text{HOCH}_3 \rightarrow \text{HOCH}_2 \rightarrow \text{HOCH} \rightarrow \text{HOC}$ or $\text{OCH} \rightarrow \text{CO}$. OH is formed by oxidation of H_2O , and then $\text{OH} + \text{CO} \rightarrow \text{HOCO} \rightarrow \text{CO}_2$. This completes the six electron oxidation. The most negative calculated reversible potential, -0.743 V, was for the first step and the most positive one, 0.494 V was for the OH forming step. The pathway involving forming methoxy as the first step is predicted to be a minority one because the reversible potential for its formation is 0.423 V.

While the calculated reversible potentials are favorable for oxidizing methanol to CO at -0.095 V, hydrogen evolution will dominate at potentials < 0.0 V. The electrode will have to be at a potential of about 0.5 V or more for OH to form and complete the oxidation of CO to CO_2 . Thus oxidation of methanol on platinum has a high overpotential.

Formic acid oxidation. The route calculated forming formic acid is $\text{OCH} + \text{OH} \rightarrow \text{HOOCH}$. This can enter the aqueous phase and at potentials greater than 0.038 V formate anion is strongly adsorbed as the formyloxy radical and $\text{H}^+(\text{aq})$ is released. Theory work of others in the literature suggests the activation energy for oxidizing the formyloxy is high. The oxidation path $\text{HOCHO} \rightarrow \text{HOCO} \rightarrow \text{CO}_2$ has favorable potentials to be a route to CO_2 . For these oxidations to occur, the electrode potential must be high enough to form OH.

Carbon dioxide reduction. The same reaction sequences for methanol oxidation can be viewed in reverse to discuss carbon dioxide reduction. On Pt(111) reduction by any path encounters a reversible potential of at least -0.7 V. This means high overpotentials would be needed to reduce carbon dioxide to methanol and, furthermore, hydrogen evolution would win in the competition for reaction sites.

Formic acid formation also suffers from very negative reversible potentials along each pathway.

The ideal methanol \rightleftharpoons carbon dioxide electro-catalyst. Using the known standard reversible potentials for oxidation and reduction of intermediates in bulk solution, one can predict the adsorption energy of each intermediate that will cause its reversible potential on the electrode surface to be the same as the standard reversible potential for the overall redox reaction. In this case the reversible potential calculated for the six-electron process involving methanol is -0.095 V and for the two-electron process involving formic acid it is -0.288 V. Methanol, formic acid, water, and carbon dioxide molecules all adsorb weakly and are assigned adsorption bond strengths zero. Beginning with these, the adsorption bond strengths which make the reversible potential of each one-electron transfer step equal to -0.095 V for the reaction involving methanol were calculated and are in the Table.

Table. Adsorption bond strengths E (eV) for the adsorbed intermediates formed during methanol on the ideal electrocatalyst. They are derived using calculated bulk solution reversible potentials and calculated adsorption bond strengths on Pt(111) at 1/6 ML coverage using the constraint that the reversible potential for each reaction step has the calculated -0.095 V six-electron reversible potential. ΔE (eV) is the increase or decrease from the values compared to adsorption on the Pt(111) surface.

Molecule	$E(\text{ads})$	ΔE
HOCO	1.998	-0.322
(HOCO)	1.805	-0.515 ^a
CO	0.533	-1.107
OCH	1.887	-0.505
HOC	3.394	-0.948
HOCH	2.635	-0.470
OCHO	2.517	0.405
(OCHO)	2.324	0.212 ^a
HOCHO ^b	0.386	0.275
HOCH ₂	1.483	-0.648
OCH ₂	1.742	-1.196
OCH ₃	1.957	-0.518
OH	2.541	0.590

a. Optimized for formic acid reaction.

b. Intermediate in six-electron reaction.

The table shows that an electro-catalyst must be found which adsorbs OH about 0.6 eV more strongly than platinum and CO about 1.1 eV more weakly than platinum. This suggests a two component catalyst. At the same time, if the route above is followed in the six-electron reaction, HOCH_2 , HOCH , and HOC must adsorb, respectively, by about 0.6 eV, 0.5 eV, and 0.9 eV more weakly than on platinum. Finding materials that cause different shifts in adsorption bond strengths is similar to the problem of improving oxygen reduction cathode electro-catalysts.¹ At the same time hydrogen evolution must not interfere.

1. A. B. Anderson, R. Jinnouchi, and J. Uddin, **Effective Reversible Potentials and Onset Potentials for O_2 Electroreduction on Transition Metal Electrodes: Theoretical Analysis**, J. Phys. Chem. C 117, 41-48 (2013)