

Dramatically Enhanced Cleavage of the C–C Bond Using an Electrocatalytically Coupled Reaction

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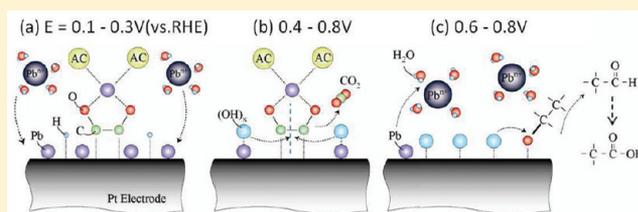
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S Supporting Information

ABSTRACT: This paper describes a generalized approach for the selective electrocatalytic C–C bond splitting in aliphatic alcohols at low temperature in aqueous state, with ethanol as an example. We show that selective C–C bond cleavage, leading to carbon dioxide, is possible in high pH aqueous media at low overpotentials. This improved selectivity and activity is achieved using a solution-born co-catalyst based on Pb(IV) acetate, which controls the mode of the ethanol adsorption so as to facilitate direct activation of the C–C bond. The simultaneously formed *under-potentially deposited* (UPD) Pb and *surface lead hydroxide* change the functionality of the catalyst surface for efficient promotion of CO oxidation. The resulting catalyst retains an unprecedented ability to sustain the full oxidation reaction pathway on an extended time scale of hours as opposed to minutes without addition of Pb(IV) acetate.



1. INTRODUCTION

The controlled electrocatalytic cleavage of the C–C bond in organic molecules, particularly in aliphatic alcohols, remains one of the most challenging problems in electrochemistry. Aside from a fundamental interest in directing a multielectron transfer to selectively cleave or form C–C bonds,¹ the reaction is also of great practical significance in the development of fuel cell-based electric energy generators.^{2,3} This implementation enabling higher alcohol oxidation can significantly improve the energy density of these low-temperature fuel cells. The inertness of the C–C bonds in electrocatalytic alcohol oxidation is counterintuitive, since the C–C bonds are relatively weak and can be, in the case of hydrocarbons, cracked either thermally or catalytically.⁴ Taking ethanol as an example, a cleavage of the C–C bond in the oxidation process leading eventually to CO₂ formation (12 electrons) is severely disfavored kinetically, especially in acid media.⁵ The electrocatalytic oxidation of aliphatic alcohols proceeds readily on Pt-based metal surfaces but usually yields just 2–4 electrons per alcohol molecule, and depending on both the electrode material and the pH, rarely involves C–C bond splitting.^{6–8} The resulting products are mostly the undesired aldehydes or corresponding acids at low pH. In contrast, in alkaline media, more complete oxidation occurs, mainly due to higher sensitivity to structural and morphological moieties such as the relative population of crystallite planes.^{9,10} Ethanol oxidation, selective to CO₂, has been reported for Pt polarized

to potentials in the oxygen evolution region in alkaline media.¹¹ The oxidation process is, however, far from controlled at these conditions.

Regardless of the media, Pt-based materials represent the benchmark catalysts for ethanol oxidation. There have been several strategies devised for enhancing the activity and selectivity of electrocatalytic ethanol oxidation,^{12–15} some based on incorporation of adatoms to the surface. The enhancement has been attributed to steric hindrance of the surface, or electronic ligand and/or bifunctional effects when the adatoms are directly involved in the catalytic process.¹⁶ The activity of purely metal-based catalytic systems is reported to be surpassed by multifunctional catalysts featuring metal oxide-based oxidation promoters like, for example, MgO,¹⁷ CeO₂,¹⁸ ZrO₂,¹⁹ or SnO_x.^{7,20} Despite the apparent improvement of the activity in the ethanol oxidation, the resulting selectivity of the oxidation process toward the desired 12 electron process still significantly lags behind expectations, with a gradual deactivation of the catalyst surface in the course of minutes. The rationalization for the C–C bond inactivity in ethanol oxidation arises because the ethanol molecule primarily adsorbs on the metal surface via the oxygen on the C₁ carbon. The first electron removed from the ethanol molecule facilitates formation of the energetically more stable aldehyde, which

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