

ETHANOL OXIDATION ON PLATINUM CATALYSTS IN ACIDIC/BASIC ELECTROLYTES

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Ethanol is one of the most promising fuels for alcohol-based fuel cells since it can be easily produced in large quantities from plant matter, is renewable, and its complete oxidation to CO_2 provides a comparably high yield of 12 electrons per molecule. Pt model catalysts are well known as highly active catalysts for oxidation of small alcohols, including ethanol. Although ethanol oxidation on Pt-based catalysts has been studied for many years, the precise reaction pathways and effects of the supporting electrolyte have yet to be fully elucidated. Based on the observation of ethanol intermediates, very simple but incomplete models of possible reaction pathways were deduced in previous studies of ethanol electrooxidation, multiple ethanol oxidation pathways occur simultaneously and often yield undesirable products and the long-lived intermediates such as CO, acetaldehyde, and acetic acid. While CO and acetaldehyde can be further oxidized to CO_2 at fuel cell relevant potentials, acetic acid cannot, and therefore constitutes a 'dead end' for the reaction. Nevertheless, the persistence of adsorbed intermediates is indicative of an incomplete ethanol oxidation and their presence significantly reduces the efficiency of ethanol-based fuel cells. In order to design more efficient fuel cells that suppress the formation of undesired intermediates such as CO and increase the selectivity of oxidations pathways

towards CO_2 formation, a molecular-level understanding of the ethanol oxidation reaction (EOR) as it occurs on the catalyst surface and the effect of the supporting electrolyte is vital. For that reason EOR has been studied previously with infrared, Raman, and vibrational sum-frequency generation (SFG) spectroscopy. However, Raman and IR studies can suffer from background issues and often struggle to disambiguate surface-adsorbed molecules from those diffused in the bulk solution. Additionally, SFG studies of EOR have been limited so far to investigations of CO vibrational bands. As a result, observations of acetaldehyde adsorbed acetyl and acetic acid or acetate have, until now, been limited to linear spectroscopic techniques.

In this paper we have applied surface specific and background-free SFG experiments to study ethanol oxidation reactions in both acidic and basic media. The SFG method of our study will be presented. We will report the first SFG spectra of adsorbed acetate and co-adsorbed sulfuric acid anions during ethanol oxidation, and the SFG studies with isotopically-labeled ethanol, which reveal significant new information on C-C bond cleavage and the behavior of adsorbed single-carbon fragments from ethanol oxidation on polycrystalline Pt.

In all SFG and electrochemical experiments a polished polycrystalline platinum disk (Matek) with a diameter of 6mm was used as working electrode. A flame-annealed platinum wire (99.99%).

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