Oxidation of glycerol: Preliminary Electrochemical Studies and Use in PEM Fuel Cells

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Introduction

The ability to oxidize higher order polyols, (e.g. glycerol) would have a profound impact on the fuel cell market. Glycerol, a waste product of biodiesel production, currently has costs associated with its disposal. In this context, we are investigating the process to electrochemically oxidize glycerol, thus, turning waste into a fuel. To make this process as efficient as possible, we are examining suitable catalysts and studying the mechanism of this oxidation process in parallel.

Substantial work has been done on electrochemical oxidation of oxygenated compounds such as methanol and ethanol. Methanol, and ‘methanol carriers’ such as tri-methoxy methane, though less active than hydrogen, are relatively easily oxidized on Pt-Ru alloys in acid media. More complex molecules such as ethanol and glycerol offer significant kinetic challenges to electrochemically rupture C-C bonds.

In this work, we present some early results on the electro-oxidation of glycerol in acid and alkaline media, followed by some fuel cell experiments.

Experimental Setup

Cyclic voltammograms were collected in a three compartment cell using a microporous counter electrode. Tests were performed using Pt, Pt0.5Cr0.5, and Pt0.87Ru.13 in both 0.5 M acidic (H2SO4) media and 0.5 M alkaline (KOH).

Fuel cell testing is conducted on a test stand configured with Fuel Cell Technologies. Subsequent exhaust gas streams are analyzed using mass spectrometry.

Results and Discussion

The reaction mechanism of glycerol will show the overall and intermediate reactions experienced during oxidation. Ex situ electrochemical voltammetry experiments are employed to obtain a first look the kinetic properties of fuels on various catalysts. Cyclic voltammetry (CV) shows the catalytic poisoning and helps identify the steps in the oxidation reaction. CVs were performed in both acidic and basic media to determine if pH have an effect on the reaction chemistry. With this knowledge we can draw conclusions regarding the oxidation process at given potentials and try to control intermediate species that poison the catalyst surface. Figures 1 and 2 are CVs from preliminary electrochemical studies in both acidic and alkaline media.

In situ fuel cell testing combined with mass spectrometry is planned to screen and quantify the reaction products of glycerol during actual fuel cell operations.

Conclusions

With the correlations between reaction mechanisms, intermediate reaction steps, catalytic poisoning, catalytic potential, and pH of the reactive environment, extensive studies can be conducted on these fuels to improve the kinetics of the intermediate and overall processes. We plan to conduct in situ fuel cell experiments to further explore the mechanisms of catalytic reactions. Other types of voltammetry, such as pulsed voltammetry may show that we are able to prevent poisoning by rapidly changing the surface potential. Real time analysis of the fuel cell exhaust streams using mass spectroscopy will allow us to isolate efficient reactions and propose better catalysts.

References