Hydrogen Generation by Electrocatalyic Reforming of Biomass-Related Compounds: Ethylene Glycol
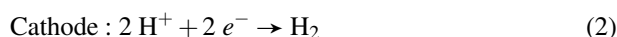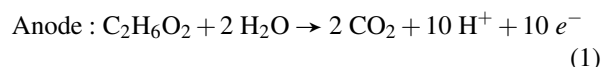
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Electrocatalytic reforming (ECR) is a promising method for generating hydrogen from biomass-derived compounds. One beneficial aspect is that hydrogen is produced at the cathode as a stream separate from the biomass mixture. In this work, we examine the feasibility of ECR for hydrogen generation. The electrocatalytic method is analogous to aqueous phase reforming (APR) [1], which has been demonstrated for a number of compounds—from ethylene glycol to glucose—at temperatures of 200–250 °C and pressures of up to 30 atm. While ECR also requires high temperatures and pressures, it should have an advantage over APR due to the influence of potential on the electrocatalyst.

Work to date has focussed on reforming of ethylene glycol, the simplest representative of a carbohydrate, to establish the efficacy of the process. The reactions of study are:

$$\text{Anode}: \text{C}_2\text{H}_6\text{O}_2 + 2\,\text{H}_2\text{O} \rightarrow 2\,\text{CO}_2 + 10\,\text{H}^+ + 10\,e^- \tag{1}$$

$$\text{Cathode}: 2\,\text{H}^+ + 2\,e^- \rightarrow \text{H}_2 \tag{2}$$

Protons formed at the anode reduce and form gaseous hydrogen at the cathode. Successful electrocatalytic reforming requires effective electrooxidation, which typically is hampered by formation of poisons at the anode [2]. The objective of this work is to examine electrooxidation at elevated temperature in aqueous phase to determine whether high temperature can reduce or eliminate poisoning.

Figure 1 shows cyclic voltammograms of EG electrooxidation in fuel cell-type reactor consisting of a 25 cm^2 symmetric membrane electrode assembly of 4 mg$_{\text{Pt}}$/cm^2 on a carbon support and a Nafion electrolyte. The pressure was kept sufficiently large to maintain a liquid phase. Ethylene glycol was fed as a 0.1 M solution, and excess hydrogen was supplied to the cathode so that it functioned essentially as a reference electrode. For reference, the reversible anode potential at 137 °C is -0.091 V$_{rhe}$.

The voltammograms exhibit little charge transfer below 0.4 V, but significant activity at higher potentials. Increasing temperatures lead to increasing current density. Notably, the hysteresis at 40 °C is essentially absent at 137 °C. Two characteristics of electrocatalytic activity are the potentials of onset and termination, E_{on} and E_{term}, respectively. In all cases $E_{term} < E_{on}$, a hallmark of CO poisoning. Adsorbed carbon monoxide forms as a partial oxidation product at potentials below about 0.6 V, and reaction cannot proceed until the CO is oxidatively removed as CO$_2$, which occurs above 0.6 V.

Figure 2 shows partial oxidation product distributions obtained by gas chromatography (GC) and high performance liquid chromatography (HPLC) analysis of the effluent gas and liquid streams. Results are shown as percentage of total products for two potentials, 0.5 and 0.7 V, and for temperatures from 40 to 137 °C. The fraction of carbon dioxide increases with temperature and is the dominant fraction
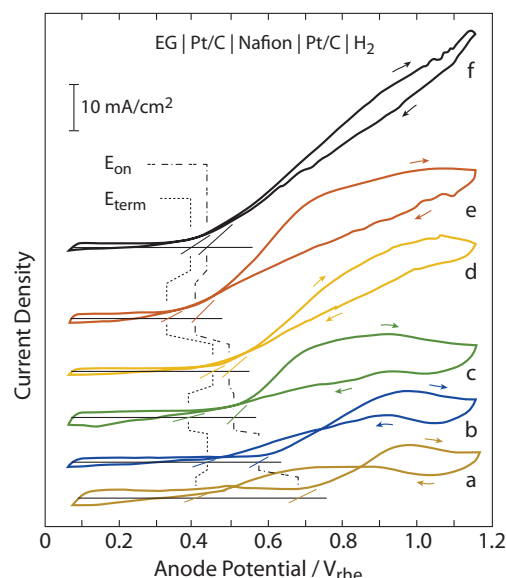
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Figure 1: Cyclic voltammograms for EG electrooxidation, with onset E_{on} and termination E_{term} potentials indicated, of 0.1 M EG on a Pt/C anode (4 mg$_{\text{Pt}}$/cm^2) at (a) 40, (b) 60, (c) 80, (d) 100, (e) 120, and (f) 137 °C.
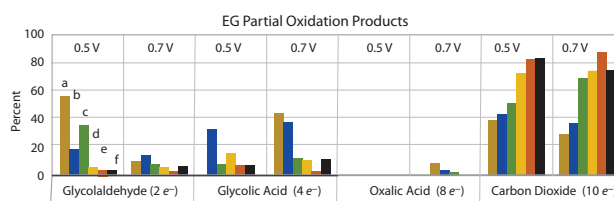

Figure 2: Partial oxidation products from EG electrooxidation as a function of potential and temperature.

at temperatures above 60 °C. Glycolaldehyde has a larger presence at 0.5 V than at 0.7 V. There is no oxalic acid at 0.5 V, but some present at lower temperatures at 0.7 V. No other species were present in significant amounts.

These results are consistent with the dual pathway mechanism. The significant amounts of CO$_2$ show that there is a more or less direct pathway to CO$_2$. The distribution of partial oxidation products shows oxidation is more advanced at higher potentials and temperatures. This is seen by progressively smaller amounts of partial oxidation products at higher temperatures. From the large amounts of CO$_2$ in both cases, we conclude that CO$_2$ is not formed from oxalic acid, but may come from other partial oxidation paths or from adsorbed CO.

ACKNOWLEDGMENTS

REFERENCES

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