

Reaction Pathways and Current Efficiency for  
Electrooxidation of Ethylene Glycol at Intermediate  
Temperatures

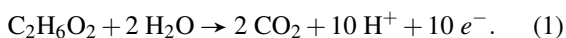
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Electrooxidation of oxyhydrocarbons, such as ethylene glycol, is central to their use for generating electricity in fuel cells or hydrogen by electrocatalytic reforming. In both cases, reaction must be performed at intermediate to high temperatures to prevent self-poisoning of the reaction and to achieve the necessary reaction kinetics. In electrocatalytic reforming, hydrogen generation is analogous to the catalytic process of aqueous phase reforming [1], which requires temperatures of 200–250 °C and pressures of up to 30 atm to maintain the liquid phase.

In this study, we report on electrooxidation of ethylene glycol on a Pt/C electrocatalyst at temperatures of up to 137 °C and pressures of up to 7 atm. The objective is to examine reaction pathways and current efficiency to identify conditions of complete oxidation, which proceeds as



Electrooxidation is hampered by formation of poisons, most notably CO, at the anode [2]. Because of the complex nature of the reactant, electrooxidation forms both partial and complete oxidation products.

Figure 1 shows several reaction pathways for products with electron transfers ranging from 2 to 10. Partial oxidation products decrease the reaction current per molecule of reactant. Current efficiency  $\epsilon_j$  is defined as

$$\epsilon_j = \frac{\sum_i N_i n_{e,i}}{n_{e,c}} \quad (2)$$

where  $N_i$  is the amount of species  $i$  formed,  $n_{e,i}$  the number of electrons transferred for species  $i$ , and  $n_{e,c}$  the number of electrons transferred for the complete oxidation product, in this case 10 for  $\text{CO}_2$ . Low current efficiency leads to low current production in a fuel cell and low  $\text{H}_2$  production in an electrocatalytic reformer.

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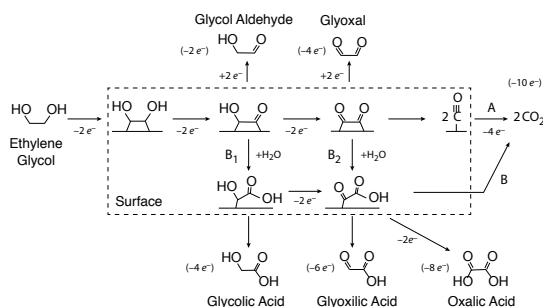


Figure 1: Reaction pathways for ethylene glycol. All species inside the dashed line box are adsorbed on the surface. All species outside the box are in the fluid phase.

The experiments were performed in a proton exchange membrane (PEM) fuel cell consisting of a 25 cm<sup>2</sup> symmetric membrane electrode assembly with Pt/C electrodes and a Nafion 117 electrolyte. Ethylene glycol was fed as a 0.1 M solution. Measurement techniques included cyclic voltammetry, potential-step (chronoamperometry), gas chromatography (GC), and high performance liquid chromatography (HPLC).

Figure 2 shows partial oxidation product distributions obtained by GC and HPLC analysis of the effluent gas and liquid streams. Results are shown as the 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 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.

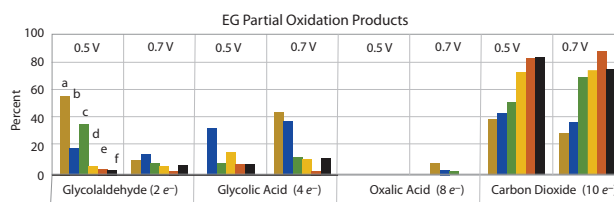


Figure 2: Partial oxidation products from EG electrooxidation as a function of potential and temperature. Temperatures of study were: (a) 40 °C, (b) 60 °C, (c) 80 °C, (d) 100 °C, (e) 120 °C, and (f) 137 °C.

The results of Fig. 2 can be converted into current efficiency, according to Eq. (2). With temperature increasing from 40 to 137 °C, the current efficiency increased approximately linearly from 0.55 to 0.90 with little dependence on potential. The essentially complete oxidation at the highest temperature studied is consistent with the absence of hysteresis in the cyclic voltammogram. From steady state reaction rates, activation energies for ethylene glycol reaction and for  $\text{CO}_2$  formation were determined to be 18 and 42 kJ/mol, respectively. The higher activation energy for  $\text{CO}_2$  formation is also consistent with increased  $\text{CO}_2$  production at higher temperatures.

These results are consistent with the dual pathway mechanism, pathways A and B in Fig. 1. The significant amounts of  $\text{CO}_2$  at low potential demonstrate the existence of pathway B. The distribution of partial oxidation products shows oxidation is more complete at higher potentials and temperatures. The increase in current efficiency follows from decreased CO poisoning (pathway A) and increased kinetics toward  $\text{CO}_2$  through both pathways.

#### ACKNOWLEDGMENTS

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#### REFERENCES

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2. H. Wang, Z. Jusys, and R. J. Behm, *Electrochim Acta*, **54**, 6484 (2009).