Renewable Energy Fuel Cell With Zero-Carbon Footprint

Tyler Young, Kayla Buhler, Steven R. Ragsdale

Curiosity: Interdisciplinary Journal of Research and Innovation

Introduction

Biofuel can be produced from any material that contains fatty acids either linked to other molecules or present as free-fatty acids. Various vegetable fats and oils, animal fats, and waste greases can be used as feedstocks for biodiesel production. Different types of reaction configurations can be employed in biodiesel synthesis including inorganic acid, inorganic base or enzymatic catalysis, biphasic or monophasic reaction systems, and ambient or elevated pressures and temperatures.

The biodiesel production process yields a crude-glycerin waste layer which is currently in global over abundance. Glycerol is the simplest example of a trihydric alcohol with three hydroxyl groups are on adjacent carbons. The terms glycerin, glycerin, and glycerol are often used interchangeably in the literature, but its official name is propane-1,2,3-triol. The primary oxidation products of glycerol are dihydroxyacetone, glyceraldehyde, hydroxyl pyruvic aldehyde and tartronic dialdehyde. Due to the multiple hydroxyl groups and their positions on the carbon chain, glycerol has the potential to form more derivatives than is usual for an ordinary alcohol. Oxidation can lead to numerous derivatives, such as glyceraldehyde, dihydroxy acetone, and glyceric aldehyde.

Technical Background

The theoretical cell voltage for a fuel cell is calculated using the standard Gibbs free energy of formation. The electrochemical potential is related to Gibbs free energy, ΔG^o, in the following equation.

$$\Delta G^o = -nFE^o \tag{1}$$

In eq. (1) n is the number of electrons involved in the reaction, F is Faraday's constant, and E^o is the standard electrochemical potential. Considering the following general cell reaction,

$$\alpha A + \beta B \rightarrow \gamma C + \delta D \tag{2}$$

the free energy change can be expressed as,

$$\Delta G = \Delta G^o + RT \ln \frac{[C]^\chi [D]^\delta}{[A]^\alpha [B]^\beta}. \tag{3}$$

When eq. (2) is substituted into eq. (3) the general form of the Nernst equation results.

$$\Delta E = \Delta E^o + \frac{RT}{nF} \ln \frac{[C]^\chi [D]^\delta}{[A]^\alpha [B]^\beta} \tag{4}$$

The Nernst equation provides a relationship between the ideal standard potential ($E°$) for the cell reaction and the ideal equilibrium potential (E) at other temperatures and partial pressures of reactants and products. For the overall cell reaction, the cell potential increases with an increase in the activity, or concentration, of reactants and a decrease in the activity of products. Therefore, in general, the voltage of a cell is expected to increase when the fuel concentration is increased.

An elementary discussion of the electrochemical principles involved in the operation of a fuel cell is available with key metrics for comparing electrochemical systems are *viz.*, energy density, power density, specific energy, and specific power (Vijh, 1980).

$$\text{Energy Density} = \text{Energy / Volume (kWh/L)} \qquad (5)$$
$$\text{Power Density } = \text{ Power / Volume (kW/L)} \qquad (6)$$
$$\text{Specific Energy} = \text{Energy / Mass (kWh/kg)} \qquad (7)$$
$$\text{Specific Power } = \text{ Power / Mass (kW/kg)} \qquad (8)$$

When comparing fuel cells, a key figure to report is the efficiency, although this is not at all a straightforward value to determine, and any value reported must be treated with caution. In the ideal case of an electrochemical converter, such as a fuel cell, the change in Gibbs free energy, ΔG^o, of the reaction is available as useful electric energy at the temperature of the conversion. The ideal efficiency of a fuel cell operating reversibly at equilibrium is given by the ratio of the change in Gibbs free energy, ΔG^o and thermal energy or enthalpy, ΔH^o.

$$\eta = \frac{Useful\ Energy}{\Delta H^o} = \frac{\Delta G^o}{\Delta H^o} \qquad (9)$$

Stated differently, the thermal efficiency of an energy conversion device, η, is the amount of useful energy produced, ΔG^o, relative to the change in stored chemical energy, ΔH^o, commonly referred to as thermal energy or enthalpy, that is released when a fuel reacts with an oxidant or is oxidized.

Direct Alcohol Fuel Cells

Current fuel cell research is primarily focused on using a polymer electrolyte membrane (PEM) as the solid-polymer electrolyte and PEMs have emerged as the technology of choice for use in low-temperature fuel cells. However, limitations associated with these membranes have hindered the commercialization and widespread acceptance of PEM fuel cells. In particular, the cost of the fuel cells is excessive due to the requirement for noble-metal catalysts. Typically, Pt and Pt-Ru alloys are used as the anode catalyst for hydrogen and methanol fuel cells, respectively, and are the main cause for the prohibitive costs for fuel cells. In addition, water-management issues arise when using proton exchange membrane and need to be addressed for methanol fuel cells. Water formed at the cathode accumulates and causes flooding. Also, fuel crossover from the anode to the cathode significantly reduces the efficiency of the fuel cell. Fuel crossover is accelerated with a proton exchange membrane from the electroosmotic flow resulting from
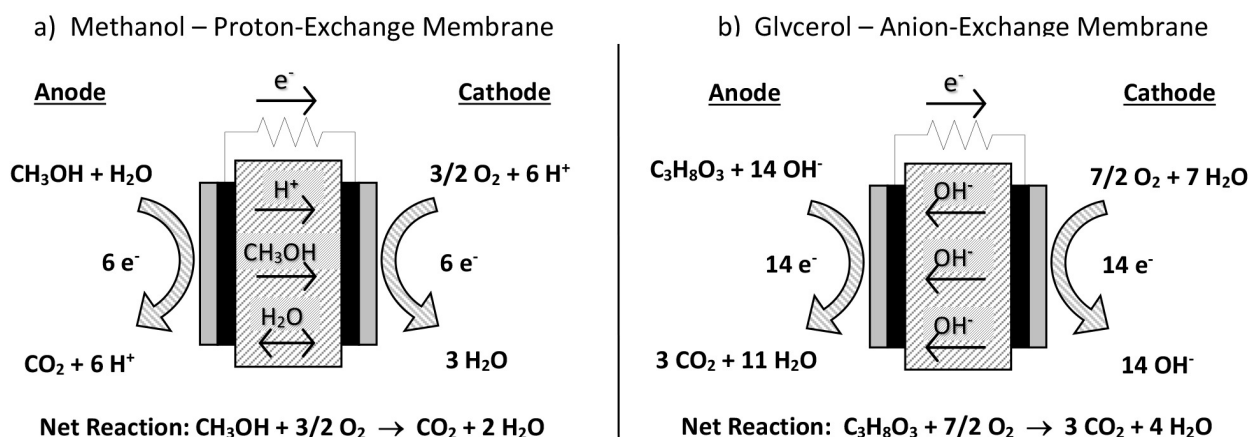
a) Methanol – Proton-Exchange Membrane

Anode   e⁻ →   **Cathode**

$CH_3OH + H_2O$ $3/2\ O_2 + 6\ H^+$

$6\ e^-$ $6\ e^-$

$CO_2 + 6\ H^+$ $3\ H_2O$

Net Reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2\ H_2O$

b) Glycerol – Anion-Exchange Membrane

Anode   e⁻ →   **Cathode**

$C_3H_8O_3 + 14\ OH^-$ $7/2\ O_2 + 7\ H_2O$

$14\ e^-$ $14\ e^-$

$3\ CO_2 + 11\ H_2O$ $14\ OH^-$

Net Reaction: $C_3H_8O_3 + 7/2\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$

Figure 1. Fuel cell reactions are depicted for a) methanol and b) glycerol using PEM and AEM, respectively.

Electroosmotic flow proceeds from the anode to the cathode in PEM fuel cells and from the cathode to the anode in AEM fuel cells. Fuel crossover and cathode flooding are amplified for PEMs compared to AEMs.

the hydrogen-ions transferring momentum to solvent and fuel molecules, imparting viscous drag, which significantly enhances mass transport across the membrane, from the anode to cathode, *see Figure 1(a)*.

Using an AAEM increases fuel cell performance and fuel efficiency for direct electrochemical oxidation of alcohols. In addition, cathode flooding is less problematic due to the electroosmotic flow resulting from hydroxyl-ion transport across the membrane that pulls water from the cathode to the anode and impedes fuel crossover, *see Figure 1(b)*. Fuel cells incorporating this membrane technology has exhibited three times the energy density compared to other diluted direct fuels, e.g., methanol, and ~10 times the energy density compared to current battery technology.

A commonly expressed concern regarding AAEMs is the stability of alkaline forms of the membranes, especially at elevated temperatures. Instability is mainly due to the displacement of the ammonium group by the OH^- anions by direct nucleophilic displacement or by Hoffman elimination when β-hydrogens are present (Xu et al., 2005). At temperatures below 60ºC membrane degradation is expected to be minimal.

A comparison of the electrochemical systems in Table 1 is used in the determination of possible fuel candidates. The analysis of the comparison of the electrical generators is based on specific energy, energy density, safety, cost and C-C bond cleavage.

The emergence of AAEM fuel cell technologies has the potential to create new markets for alternative direct fuels. Several alternative fuels for direct fuel cells have been investigated, including dimethyl ether (Muller et al., 2000), glycerol (Matsuoka et al., 2005), ethanol (Xu et al., 2005), and ethylene glycol (Smirnova et al., 1988). Polyhydric alcohols such as ethylene glycol and glycerol are much less volatile and less toxic than methanol. Experimental evidence of substantially higher efficiencies using an AAEM fuel cell has been demonstrated in our laboratory.

Table 1. Thermodynamic and Electrochemical Data for Alternative Fuel Candidates (Lange, 1967)

Alcohol	Formula	ΔG^O (kJ/ mol)	ΔH^O (kJ/ mol)	n	E^O_{cell} (V)	Specific Energy (kWh/kg)	Energy Density (kWh/L)
Methanol	CH_3OH	-702	-726	6	1.21	6.1	4.8
Ethanol	C_2H_5OH	-1325	-1367	12	1.15	8.0	6.3
Propanol	C_3H_7OH	-1853	-2021	18	1.07	8.6	6.8
Oxalic Acid	$C_2H_2O_4$	-329.7	-252	2	1.71	1.0	1.9
Dimethyl Ether	C_2H_6O	-1362	-1328	12	1.18	8.2	5.5
Ethylene Glycol	$C_2H_6O_2$	-1183	-1177	10	1.22	5.3	5.9
Glycerol	$C_3H_8O_3$	-1646	-1661	14	1.22	5.0	6.3

To fully oxidize glycerol to CO_2 involves 14 electrons. Although, the reactants will only be partially oxidized at the anode electrocatalysts. The exact number of electrons transferred depends on the catalyst composition, nanostructure, and the fuel cell operating voltage and temperature.

Sequential oxidation of glycerol in alkaline media leads to carboxylation of one or both of the terminal carbons resulting in a partial electrooxidation reaction.

$$C_3H_8O_3 + 8OH^- \rightarrow C_3H_4O_5 + 6H_2O + 8e^- \qquad (10)$$
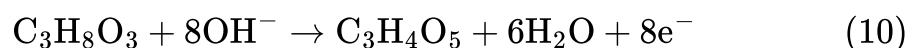
This is an example of an 8-electron transfer reaction, but there are dozens of alternative partial oxidation pathways (involving as many as 10 electrons) that do not result in carbon-carbon bond scission.

Recently there has been increased research on the preparation and properties of AAEMs. AAEM have application in dialysis, water treatment and purification. A general classification of polymeric materials potentially suitable for use in alkaline fuel cells (Gottesfeld et al., 2018), and of their specific properties is available (Lin et al., 2014). The backbone stability of benzyl-trimethyl ammonium functionalized polyaromatics is important for stable, durable membranes for use in AAEM fuel cells (Xu et al., 2005) Backbone degradation significantly reduces the mechanical properties of the membranes and reduces hydroxide conductivity (Fujimoto et al., 2012).

Ammonium-type anion exchange membranes composed of fixed cation groups, such as tetra-alkyl ammonium groups, bonded to a polyolefin backbone chain are used as the polymer electrolyte membrane. The Cl⁻ form of the membrane or electrolyte is converted to the OH⁻ form by immersion in a 1 M KOH aqueous solution at 40ºC for 2 hours or room temperature for 24 hours to exchange Cl⁻ with OH⁻. The membranes are washed in a final rinse of water and are then ready to use.

Fuel Cell Assembly and Performance

Membrane Electrode Assemblies (MEAs) with an AAEM can use supported and unsupported catalysts deposited on carbon electrodes. The anode and cathode are separated by the AAEM. The MEA is fabricated by

heat pressing the anode, cathode, and membrane at 65°C and 200 psi. After heat pressing the electrodes are inspected for good bonding and to verify that the electrodes are not shorted.

Fuel cells with 25-cm^2 active surface area MEAs were assembled. Polarization curves were obtained for fuel cells with AAEM electrode assemblies and glycerol as fuel. Catalyst loading ranged from 1-3 mg/cm^2 Pt-Ru for the anode and 0.5 mg/cm^2 Pt for the cathode.

The fuel cell uses an air cathode that reduces ambient oxygen. The anode compartment is equipped with a reservoir and contains the fuel. Seals and gasketing are inert materials that exhibit excellent electrical and thermal properties.

The polarization curve is perhaps the most familiar test to assess cell performance. A characteristic cell voltage vs. load curve is generated by introducing different electrical loads on the fuel cell. Polarization and power curves for an AAEM fuel cell has shown that fuel cell performance is limited by kinetic, resistive, and mass transfer losses. By improving the catalyst gains of 100 mV or more are observed in alkaline solutions at low current conditions. In addition, more than a 100-mV gain is observed by improved MEA production methods. These gains can boost the peak power from 100 mW to >180 mW, resulting in performance (>600 mW) and the energy (voltage >400mV for >0.5 Wh/mL) that is required for viable commercialization of this technology.

Conclusion

A direct-fuel cell using a novel membrane and fuel cell configuration has demonstrated 5-10x greater energy density compared to typical direct-methanol fuel cells (DMFCs). The AAEM increases the efficiency by 20-30% compared to using a proton-exchange membrane. The fuel cell has an open-circuit potential 100-200 mV greater than typical DMFCs. The enhanced fuel cell performance is described by mass transport, electrode kinetics, and concentrated fuel. Our results using glycerin showed only a minimal decrease in performance for concentrated solutions up to 60%.

References

Fujimoto, C., D-S, K., Hibbs, M., Wrobleski, D., & Kim, Y. S. (2012). *Journal of Membrane Science*, *423–424*, 438–449.

Gottesfeld, S., Dekel, D. R., Page, M., Bae, C., Yan, Y., Zelenay, P., & Kim, Y. S. (2018). Anion exchange membrane fuel cells: Current status and remaining challenges. *Journal of Power Sources*, *375*, 170–184. https://doi.org/10.1016/j.jpowsour.2017.08.010

Lange, N. A. (1967). *Lange's Handbook of Chemistry* (10th ed.). McGraw-Hill.

Lin, B., Chu, F., Ren, Y., Jia, B., Yuan, N., Shang, H., Feng, T., Zhu, Y., & Ding, J. (2014). Alkaline stable C2-substituted imidazolium-based cross-linked anion exchange membranes for alkaline fuel cell applications. *Journal of Power Sources*, *266*, 186–192. https://doi.org/10.1016/j.jpowsour.2014.05.003

Matsuoka, K., Iriyama, Y., Abe, T., Matsuoka, M., & Ogumi, Z. (2005). Alkaline direct alcohol fuel cells using an anion exchange membrane. *Journal of Power Sources*, *150*, 27–31. https://doi.org/10.1016/j.jpowsour.2005.02.020

Muller, J. T., Urban, P. M., Holderich, W. F., Colbow, K. M., Zhang, J., & Wilkinson, D. P. (2000). *Journal of The Electrochemical Society*, *147*, 4058.

Smirnova, N. W., Petrii, O. A., & Grzejdziak, A. (1988). *Journal of Electroanalytical Chemistry*, *251*, 73.

Vijh, A. K. (1980). Electrochemistry, power sources and energy science. *Journal of Power Sources*, *5*(2), 145–172. https://doi.org/10.1016/0378-7753(80)80104-2

Xu, C. W., Shen, P. K., Ji, X. H., Zeng, R., & Liu, Y. L. (2005). *Electrochemistry Communications*, *7*, 1305.