Electrocatalytic conversion of biorenewable feedstocks for electricity and chemicals cogeneration in anion exchange membrane fuel cells

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Electrocatalytic conversion of biorenewable feedstocks for electricity and chemicals cogeneration in anion exchange membrane fuel cells

by

Neeva K. Benipal

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

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The student author and the program of study committee are solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alternations after a degree is conferred.

Iowa State University

Ames, IA

2017

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To my both grandfathers, Raghibir S. Benipal and Surjit S. Gill
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ACKNOWLEDGMENTS

First and foremost, I would like to express my deepest gratitude to Dr. Wenzhen Li for the opportunity to work in his group at Iowa State University. He has provided me with constant encouragement, patience, and guidance at different stages of my research, and his enthusiasm for research combined with his wonderful work ethic have taught me to greatly appreciate his depth of knowledge and his kindly demeanor towards all his students. I am grateful to my POS committee members, Dr. Jean-Philippe Tessonnier, Dr. Robert C. Brown, Dr. Eric W. Cochran, and Dr. Wenyu Huang for their valuable advice and providing helpful feedback and suggestions related to this dissertation. I am particularly thankful to our collaborators, Dr. Robert C. Brown and Patrick A. Johnston, and would also like to extend my warm thanks to all other faculty and staff in the Department of Chemical and Biological engineering at Iowa State University. I am thankful for my funding sources including the National Science Foundation (CBE 1159448 and 1501124), the Iowa State University Startup Fund, the Iowa Energy Center Opportunity Grant, and the Ames Laboratory Startup Fund.

I would like to thank the past and present members of Li’s group: Dr. Ji Qi, David Chadderdon, Yang Qiu, and Xiatong Chadderdon. In particular, I would like to acknowledge Ji Qi for his guidance and supervision during my first year of graduate school, his invaluable encouragement, and, most importantly, his friendship during the remainder of my graduate school study. I have also had the good fortune of having committed undergraduate students working with me, and I would dearly like to thank all my undergraduate students: Jacob C. Gentile, Darcie H. Farrell, Qi Liu, Ryan F. McSweeney, and Baitong Chen. The lab would
...have had been a very isolated place without them all. They have been more like friends who made going through the occasional woes and frustrations of the lab much easier.

I am indebted to friends that I have made both inside and outside of CBE both at Iowa State University and Michigan Technological during the last 5 years. There are too many to name here but I sincerely express my thank you to all for being through with me together through both good and bad times, cheering me up and supporting me with endless love and strength, and helping me to take shape into the person I wanted to be. I would also like to express my gratitude to Tom Munie and the Haider family for considering me as a family member and for their continuous support since the first day I began working on this degree. I could not possibly thank them enough. Finally, and most importantly, I would like to express my special gratitude to my family for giving me unconditional love, support, and strength through all these years.
ABSTRACT

Continuing depletion of world’s fossil fuel resources has been a driving factor for seeking an ultimate goal of reducing heavy US dependence on fossil fuels by extensively investigating and developing alternative fuel sources and technologies including biorefinery use of lignocellulose biomass. Electrochemistry and electrocatalysis based technologies have great potential to be used in the next generation of biorefineries, part of developing sustainable technologies to mitigate global warming and lower dependence on fossil fuels. Electrical energy could be directly generated using electrochemical fuel cell reactors based on electrocatalytic conversion processes. This might be a promising green route to partially alleviating our energy dependence on traditional fossil fuel resources. Although great progress has been achieved in selective catalytic conversion of biorenewable compounds in heterogeneous catalysis, there is still a need to explore and develop electrocatalytic biorefineries to selectively produce valuable chemicals while simultaneously generating electricity. The research efforts described in this Ph.D. dissertation are divided into two parts: applied fundamental electrocatalysis research and practical direct biorenewable fuel cell technologies development.

First, electrocatalytic oxidation of biorenewable polyols (C₃ glycerol and C₄ meso-erythritol) for valuable chemicals and electricity cogeneration has been investigated on supported Pd-based nanoparticle electrocatalysts in alkaline anion-exchange membrane fuel cells. PdAg bimetallic nanoparticle catalyst has been shown more efficient than Pd for alcohol oxidation due to Pd facilitating deprotonation of alcohol in a base electrolyte, while Ag promotes intermediate aldehyde oxidation and cleavage of C-C bond of C₃ species to C₂ species. A mechanistic understanding of electrocatalytic oxidation of glycerol and meso-erythritol and associated bond breaking on PdAg bimetallic catalysts has been developed, and the keys influencing product
distribution and reaction pathways were further elucidated and controlled by optimizing electrocatalysts and reaction conditions.

The second part of this dissertation describes the development of practical biorenewable fuel cells technologies focused on alternative “fuel” and inexpensive durable “cells” (device). A new route for directly using complex biomass derived bio-oil as an alternative fuel to generate electricity in alkaline membrane fuel cells has been explored. Electrochemical performance of bio-oil derived from the pyrolysis of lignocellulosic biomass over precious metal monometallic catalysts such as Pt/CNT, Pd/CNT, Au/CNT, and Ag/CNT has been studied. In order to reduce costs and improve durability of fuel cell devices, the usage of porous polytetrafluoroethylene (PTFE) thin films as separators in high alkaline direct glycerol fuel cells has been thoroughly investigated. Low-cost, stable and durable PTFE thin film separators have demonstrated superior performances compared to state-of-the-art anion exchange membranes with respect to anode degradation in alkaline fuel cells under harsh alkaline conditions. Our preliminary work on integration of carbon-based cathode catalyst, porous PTFE thin film separator, and crude biorenewable fuel into a fuel cell device to generate low cost bio-electricity has shown promise toward the development of novel alkaline fuel cells with high performance, low cost, and desired durability.
CHAPTER 1 BACKGROUND AND SIGNIFICANCE OF THE RESEARCH

1.1 Introduction

Fossil fuels are currently the world’s primary energy source. Based on U.S. energy flow in 2015, fossil fuels, including petroleum (35.4%), coal (15.7%), and natural gas (28.3%), supplied 79.4% of total energy consumption. Fossil fuels reserves are well known to be finite. According to the CIA World Factbook on fossil fuel reserve and consumption, over 11 billion tons/year of oil are consumed globally. Crude oil reserves are also vanishing at the rate of 4 billion tons/year. The rapid growth of the global population, rising living standards, and the world’s rate of fossil fuel consumption are placing additional demand on energy supplies. The dwindling supply of fossil fuels and, more importantly, air quality deterioration, and global climate change due to burning fossil fuels and release of global greenhouse gases into the environment, have become serious concerns.

Fig. 1.1 Fossil fuel reserve and consumption data from CIA World Factbook.
Future energy demand along with preservation of a clean environment for future generations motivate us to shift our focus from exploiting fossil fuels to developing more affordable, reliable, and clean energy sources. Sustainable energy has unique significance but its adoption has been identified as a top challenge for the next fifty years. Based on the Renewable energy policy network for the 21st century (REN21)’s 2014 report, renewable sources contributed 19% to global energy consumption, divided into 9% coming from traditional biomass, 4.2% as heat energy, 3.8% hydroelectricity, and 2% is electricity production from wind, solar, geothermal, and biomass. Liquid biofuels from renewable lignocellulosic biomass has the potential to significantly reduce our dependence on fossil fuels and alleviate greenhouse gas emission, so biofuels can be considered as alternative fuel sources for the future energy supply landscape. The biomass-based biorefinery industry has the potential to replace petroleum-based refinery industries, meeting the needs of energy, chemicals, and clean environment.

Fig. 1.2 Total world energy consumption by source conducted by 2013.
1.2 Biorefinery

A biorefinery is a sustainable processing facility that integrates a wide range of different biomass feedstocks into bio-based products such as food, value-added chemicals, feed, and materials and bioenergy (biofuels, power output, and/or heat). Effective usage of biomass resources largely relies on development of modern biorefinery processes that employ biological, chemical, and thermal approaches to converting biomass to biofuels [1-3]. According to the U.S. Energy Information Administration (EIA), the current cost of lignocellulosic biomass ranges from $5 to 15 boe (barrels of oil energy equivalent), significantly lower than the crude oil price of $97/bbl (per barrel) averaged in 2013 [4]. Biomass resources are annually renewable, cheap, and abundant. Global biomass demand is expected to significantly increase in our future energy landscape during the interval 2005 to 2050 [5]. The U.S. Department of Energy (DOE) has identified the top 12 platform molecules (Table 1.1) that can be obtained from the established biorefinery processes that represent great potential to serve as building blocks for future production of polymers, foods, chemical, pharmaceuticals, etc.

Table 1.1 The 12 sugar-based building blocks selected by DOE [6].

<table>
<thead>
<tr>
<th>1,4 diacids (succinic, fumaric and malic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5 furan dicarboxylic acid</td>
</tr>
<tr>
<td>3 hydroxy propionic acid</td>
</tr>
<tr>
<td>aspartic acid</td>
</tr>
<tr>
<td>glucaric acid</td>
</tr>
<tr>
<td>glutamic acid</td>
</tr>
<tr>
<td>itaconic acid</td>
</tr>
<tr>
<td>levulinic acid</td>
</tr>
<tr>
<td>3-hydroxybutyrolactone</td>
</tr>
<tr>
<td>glycerol</td>
</tr>
<tr>
<td>sorbitol</td>
</tr>
<tr>
<td>xylitol/arabinitol</td>
</tr>
</tbody>
</table>
The Environmental Protection Agency (EPA) has recognized biodiesel by classifying it as an advanced biofuel, making biodiesel the only commercial-scale U.S. fuel produced nationwide. Annual production of biodiesel has increased from about 25 million gallons in the early 2000s to about 1.7 billion gallons in 2014. Biodiesel is obtained from natural lipids such as vegetable oil or animal fat using industrial processes called transesterification that converts oil and fats into chemicals called long-chain mono alkyl esters that are given the name biodiesel, with glycerin (glycerol) as a co-product. The blooming biodiesel industry can lead to a surplus in glycerol production; utilization of glycerol for producing larger volumes of fine chemicals and fuel additives can attract industrial interest in the market. The production of bio-ethanol also generates glycerol, up to 10% of the weight of sugar consumed, as a by-product [7]. Glycerol, is a model biorenewable simple polyol compound that is colorless, odorless, and non-toxic; it consists of three-carbon alcohol with three hydroxyl groups attached. Glycerol is commonly used in the food industry as a sweetener, and in medical, pharmaceuticals, and cosmetics applications [8].

Creating a biorefinery based on pyrolysis of biomass represents an important step in the transition towards a sustainable economy. Pyrolysis bio-oil has also been suggested as a building block for our future production of chemicals and fuels. Fast pyrolysis is a rapid thermal decomposition of organic compounds (biomass, a natural product that contains carbon) in the absence of oxygen to produce pyrolysis liquid (bio-oil), char, and gases. Pyrolysis liquid, also known as bio-oil, is a low viscosity, dark-brown fluid with up to 15 to 20% water content. Pyrolysis of cellulose goes through both fast and slow multiple reaction pathways. Fast pyrolysis of cellulose goes through depolymerizatin and alkali-catalyzed
dehydration reaction pathways to produce levoglucosan, hydroxyacetaldehydes. Slow pyrolysis of cellulose provides char and water as end products. Advantages of fast pyrolysis are that it operates at atmospheric pressure and modest temperature (450°C) and yields of bio-oil can exceed 70 wt%. Disadvantages are that high oxygen and water content of bio-oil makes it inferior to conventional hydrocarbon fuels; in addition, polymerization of liquids and corrosion of containers make storage of these liquids difficult. A wide variety of biomass feedstocks can be used in the production of bio-oil. The transformation of bio-oil has been actively explored in applications such as post processing of motor fuels through direction application of bio-oil, hydrocracking, gasification, and fermentation of bio-oil [9]. The development of renewable biomass-derived fuels (glycerol and bio-oil) are interesting topics for achieving sustainable development.

1.3 Electro-biorefinery: Fuel Cells

There is a need to develop new technologies for generating electricity from biorenewable feedstocks and for renewable electricity storage to improve the efficiency of current renewable electricity generation processes. Electrochemical/Electrocatalytic processing of biomass-derived oxygenated compounds to chemicals, liquid fuels, and electricity in electrochemical cells (including fuel cell and electrolysis cell) may thus play a significant role in this regard. Fuel cells are environmentally friendly devices for energy conversion, power generation, and are generally regarded as one of the promising advanced energy technologies of the future. Fuel cells can directly convert chemical energy stored in chemical bonds of a fuel into electrical energy. Today’s fuel cells have capability to ensure energy security, high efficiency, low operating cost, fuel versatility, and pollution-free power [10, 11]. Fuel cell can operate isothermally, so less energy is lost in maintaining the
temperature of the “hot source”, making fuel cells less irreversible. However, because of
the absence of temperature cycling, a fuel cell does not follow the Carnot cycle, and is
therefore not limited by the Carnot efficiency. Fuel cells do not conform to Carnot’s
theorem, therefore, higher energy efficiencies than those of combustion engines can be
expected, i.e., up to 40-50% in electrical energy and 80-85% in total energy (heat +
electricity). In addition, fuel cells can be used in variously-scaled stationary and mobile
systems for quiet and continuous power generation [12]. Fuel cells can vary from small
devices producing only a few watts of electricity up to large power plants producing
megawatts. The electrochemical reactions in the fuel cell’s anode and cathode electrodes
produce direct current (DC) power that can be converted to alternating current (AC) power
using devices such as inverters.

In general, fuel cells can be classified into several categories, as listed in Table 1.2:
Polymer Electrolyte Membrane Fuel Cell (PEMFC), Alkaline Fuel Cell (AFC), Phosphoric
Acid Fuel cell (PAFC), Molten Carbonate Fuel Cell (MCFC), and Solid Oxide Fuel Cell
(SOFC), and many more. The classification of fuel cells is primarily by the nature of the
electrolyte and charge carrier they employ. This classification helps to determine the kind of
electro-chemical reactions taking place in the cell, the catalysts required, the operating
temperature, the fuel required, and other factors. The advantages of fuel cells are their
capability for providing high efficiency, clean and carbon free energy when using H₂ and
O₂, using renewable fuels, with no moving parts, no noise, continuously operation as long
as fuel is available, and highly scalable to applications ranging from cell phones to power
plants. The disadvantages of fuel cells are high cost due to expensive materials like Pt, low
density of fuel compared to gasoline, poor durability at high temperatures, and catalyst
contaminations. Among the different types of fuel cells, proton-exchange membrane fuel cells (a type of PEMFC, polymer electrolyte membrane fuel cell) feature prominently in the contemporary literature. Their small size and high efficiency has made them ideal candidates for automotive applications; in fact, the use of PEMFCs dates back to the first NASA space programs.

Table 1.2 Conventional comparison of fuel cells.

<table>
<thead>
<tr>
<th></th>
<th>PEMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrolyte</strong></td>
<td>PEM (proton exchange membrane)</td>
<td>AEM (anion exchange membrane)</td>
<td>Liquid KOH</td>
<td>Liquid H₃PO₄</td>
<td>molten carbonate salt</td>
</tr>
<tr>
<td><strong>Charge carrier</strong></td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>CO₃²⁻</td>
</tr>
<tr>
<td><strong>Typical working Temperature (°C)</strong></td>
<td>50-100</td>
<td>50-100</td>
<td>50-100</td>
<td>150-200</td>
<td>600-700</td>
</tr>
<tr>
<td><strong>Common Catalyst</strong></td>
<td>Platinum</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel</td>
</tr>
<tr>
<td><strong>Fuel compatibility</strong></td>
<td>H₂, alcohol</td>
<td>H₂, alcohol</td>
<td>H₂</td>
<td>H₂</td>
<td>H₂, CH₄</td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
<td>50-60% electric</td>
<td>50-60% electric</td>
<td>60-70 % electric</td>
<td>80-85 % overall</td>
<td>85% overall</td>
</tr>
<tr>
<td></td>
<td>36-42% electric</td>
<td>60% electric</td>
<td>60% electric</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>System output</strong></td>
<td>&lt;250kW</td>
<td>&lt;250kW</td>
<td>10kW-150kW</td>
<td>50kW–1MW</td>
<td>&lt;1MW</td>
</tr>
</tbody>
</table>

A typical PEMFC can work stably at low temperatures (<100°C) while maintaining a power generation capability of up to 250 kW [13]. However, the cost involved in the high
loading of platinum-group catalysts, and the stringent H₂ gas storage/transport infrastructure requirements make the H₂ fuel cell less competitive. While intensive research studies are in progress, direct alcohol fuel cells (DAFCs) have attracted enormous attention as potential power sources, mainly because alcohol as a liquid fuel is derivable from annually renewable biomass, easy to transport, and convenient to store [14]. However, challenges such as poor oxidation kinetics at the anode, fuel purity requirements, and alcohol crossover issues limit widespread practical applications of DAFCs technology. Alkaline anion exchange membrane fuel cells (AEMFCs) have recently emerged quickly as a potential solution to these problems. The electrocatalytic kinetics of both anode (fuel oxidation) and cathode (oxygen reduction) are higher in an alkaline media compared to an acid media due to facile charge transfer and enhanced ion transport [15, 16]. Furthermore, the poison severity of impurities and contaminants on anode catalysts can be greatly alleviated in alkaline environments [17]. A high pH environment also allows the participation of low cost non-platinum catalysts, thereby reducing the cost of the fuel cells; also, products including carbonate of AEM-DAFCs remain in the aqueous solution with zero environmental impact [18]. In addition, at the cathode side, a relatively cheaper non-platinum catalyst can provide faster kinetics for an oxygen reduction reaction (ORR) in AEMFC than in PEMFC. An alkaline electrode membrane for AEMFCs is also cheaper than an acid electrolyte membrane (e.g. Nafion) because solid AEMs have no fixed cations and exhibit a distinct OH- transfer and diffusion behavior compared to a liquid base solution. The volumetric energy densities of ethanol and glycerol are also higher than that of H₂ (6.3 kW hL⁻¹ for ethanol and glycerol vs. 2.6 kW h L⁻¹ for H₂). Because of these traits, DAFC fed with biomass-derived alcohols will be a promising high-efficient, cost-effective power generation technology. To explore
more alternative fuels, several studies have been carried out based on the AEMFC platform using biorenewable fuels such as glucose [19], cellulose [20], and crude glycerol [21]. There is an urgent need to seek widely available and economical biomass-derived oil/fuels for fuel cell applications.

1.4 Selective catalytic oxidation of polyols and sugars

Electrocatalytic selective oxidation of biorenewable alcohols to valuable chemicals, liquids, fuels, over metal catalysts with molecular oxygen is a very attractive green process. Electrocatalysis plays a central role in developing a green technology in being responsible for the adsorption of reactants, activation and stabilization of intermediates and desorption of the products [22-24]. Recently, great progress have been made in heterogeneous catalysis in selective oxidation of glycerol to tartronate [25], mesoxalate [26], and dihydroxyacetone [27, 28]. The catalyst structure, support, size, reaction conditions (e.g., temperature, O\textsubscript{2} pressure, pH, ratio of catalyst to glycerol, O\textsubscript{2} or H\textsubscript{2}O\textsubscript{2} as oxidant) influence the selectivity of reactivity [29-33]. Because reaction kinetics and pathways of a reaction can be enhanced under an applied potential, the electrocatalytic conversion of glycerol should be of exclusive significance by being more efficient, and eco-benign. Au has been shown to improve the selectivity of glyceric acid (65% selectivity) at glycerol conversion of 33% under optimized conditions [29]. Furthermore, Pd has been reported to facilitates oxidation to tartronic acid [32]. Bimetallic catalysts significantly promote catalytic activity for the electro-oxidation of glycerol and also reduce the cost of the anode catalyst. The kinetics of alcohol oxidation can be greatly enhanced in high pH media [29, 33, 34]. According to density functional theory (DFT) calculations, the activation energies of the first dehydrogentation step in the absence
of OH- are as high as 2014 and 116 kJ/mole for Au and Pt catalysts, respectively, while they drop to 22 and 18 kJ/mole for both Au and Pt with the assistance of base (OH-) [29].

Recently, AEM-DAFCs have been demonstrated to be an electrochemical reactor for cogeneration of electricity and useful chemicals from polyols, as illustrated in Fig. 1.3. A typical fuel cell is divided into three main constituent parts, i.e., the anode, the cathode, and a membrane. During the electrochemical process, at the anode, fuel, for instance glycerol, is fed and reacts with OH- to produce CO₂ (complete oxidation) or valuable chemicals (e.g. tartronate). At the membrane, OH⁻ ions travel through from the cathode to the anode electrode. Electrons are ejected from the fuels out of the cell through an electrical circuit to generate electricity. At the cathode, the ejected electrons recombine with O₂ and H₂O to form OH⁻ ions which transport to anode. The product distribution of an alcohol oxidation is investigated by continuously looping fuel (alcohol in KOH solution) from a plastic vessel into the anode, while a constant cell operation voltage was applied at a certain temperature and time. The liquid products are analyzed using analytical techniques, such as HPLC, HPLC-MS and NMR.

![Fig. 1.3 Schematic of Alkaline AEMFC with polyol fuels.](image-url)
Complete oxidation:

Anode: $\text{C}_3\text{H}_8\text{O}_3 + 20\text{OH}^- = 3\text{CO}_3^{2-} + 14\text{H}_2\text{O} + 14\text{e}^-$

Cathode: $3.5\text{O}_2 + 7\text{H}_2\text{O} + 14\text{e}^- = 14\text{OH}^-$

Overall: $\text{C}_3\text{H}_8\text{O}_3 + 3.5\text{O}_2 + 6\text{OH}^- = 3\text{CO}_3^{2-} + 7\text{H}_2\text{O}$

(-0.968 vs SHE)  
(0.401 V vs. SHE)  
($E^0 = 1.369$ V)

Partial oxidation (tartronate product as an example):

Anode: $\text{C}_3\text{H}_8\text{O}_3 + 10\text{OH}^- = \text{C}_3\text{H}_2\text{O}_5^{2-} + 8\text{H}_2\text{O} + 8\text{e}^-$

Cathode: $2\text{O}_2 + 4\text{H}_2\text{O} + 8\text{e}^- = 8\text{OH}^-$

Overall: $\text{C}_3\text{H}_8\text{O}_3 + 2\text{O}_2 + 2\text{OH}^- = \text{C}_3\text{H}_2\text{O}_5^{2-} + 4\text{H}_2\text{O}$

(-0.908 V vs. SHE)  
(0.401 V vs. SHE)  
($E^0 = 1.309$ V)

The scarcity and cost of traditional Pt metal for both anode and cathode catalysts is a serious challenge to widespread fuel cell applications, so extensive efforts have been taken to explore other efficient and durable catalysts [35-47]. Stable and efficient fuel-cell electrocatalysts, however, have been extensively investigated. A traditional way of approaching this problem is to reduce the amount of Pt by replacing Pt with an efficient metal catalyst, adding bimetallic composition to Pt content or adjusting support combinations of Pt with other materials. Morphology of a catalyst can also play an important part in catalytic and electrocatalytic reactions. Pd, an important noble metal to substitute Pt due to its richer reserve on earth and lower price, has traditionally been used for various catalytic applications, particularly, in the electronics, and petroleum cracking industries, and for hydrogen storage applications. Recent studies have shown that catalysts consisting of two metals (bimetallic) allow greater reactivity and more flexible design [48, 49]. Using computational approaches, it is possible to screen a second metal to assist noble metal to achieve better electrocatalytic functions.
1.5 Research Objectives

Our group has previously demonstrated that glycerol can deliver high power density as well as valuable glycerol oxidation products in AEMFC via rationale design electrocatalysts and optimization of fuel cell operation conditions. This provides me with a solid base as well as a unique opportunity to further study electrocatalytic oxidation of glycerol and extend it to C₄ polyol meso-erythritol. My Ph.D. work firstly focused on applied fundamental electrocatalysis research, including 1) investigation of the relationship of bimetallic Pd-Ag nanoparticle catalyst structure and composition and their electrocatalytic oxidation of polyol, and 2) elucidation of reaction pathways/mechanisms of selective electrocatalytic oxidation of C₃ and C₄ polyols; and then focused on practical direct biorenewable fuel cell technologies development, including: 1) exploration of membrane-free separator based alkaline fuel cell with inexpensive cathode catalysts (non-precious metal or metal-free) for oxygen reduction reaction, 2) exploration of direct pyrolysis bio-oil fuel cells using alkaline membrane platform.

In detail, the topics of my Ph.D. research are:

1) Investigate electrocatalytic oxidation of biorenewable organic molecules such as C₃ glycerol (Chapter 3) and C₄ meso-erythritol (Chapter 4) for valuable chemicals and electricity cogeneration on supported Pd-based nanoparticle electrocatalysts in alkaline anion-exchange membrane fuel cells. Develop an understanding of PdAg/CNT on electrocatalytic oxidation of glycerol and meso-erythritol and associated bond breaking, and study keys that influence product distribution and a reaction pathways mechanism to be controlled through electrocatalysts and the reaction conditions.
2) Explore a new route for using complex biomass derived bio-fuels such as bio-oil as a generalized approach for alternative fuels in fuel cell applications to generate electricity (Chapter 5). Study the electrochemical performance of bio-oil derived from the pyrolysis of lignocellulosic biomass over model precious metal catalysts such as Pt/CNT, Pd/CNT, Au/CNT, and Ag/CNT. Low-cost bioethanol, biodiesel waste glycerol, and bio-oil can serve as promising fuels in direct liquid fuel cells.

3) Study porous polytetrafluoroethylene (PTFE) thin films as a separator in high alkaline for DGFCs (Chapter 6). Exploration of new, low-cost, stable, and durable PTFE thin film separator and comparison of the state-of-the-art ion-selective membranes, and research on anode degradation under harsh alkaline conditions in alkaline fuel cells. The practical research goal is to integrate cheap carbon-based cathode catalyst, porous PTFE thin film separator and crude biorenewable fuel to generate low cost bio-electricity.

1.6 References


2.1 Abstract

Electrocatalysis is an emerging technology for biomass conversion and is anticipated to play an increasingly critical role in production of sustainable energy. Biomass and biomass-derived compounds are widely recognized as playing a significant role as the only sustainable source of carbon that can be used to produce renewable fuels and valuable chemicals. This review discusses the status and challenges of electrocatalytic oxidation of bio-based glycerol compounds that have primary targeted common functionalities: hydroxyl group. The important reaction parameters including electrode catalysts, electrode potential, electrolyte, reaction mechanisms, and including their thermodynamics are reviewed. Current challenges and future opportunities are also discussed.

* The material contained in this chapter was adopted from a review manuscript that is under preparation for its publication.
2.2 Introduction

In recent years, tremendous interest has been directed toward using renewable and clean energy sources to alleviate global climate change and environmental pollution through reducing or eliminating use of fossil fuels. These concerns have given us an impetus to explore other alternatives, especially more affordable, reliable, and clean energy sources. Biomass and biomass-derived compounds are widely recognized for playing a central role as the only sustainable source of carbon that can be used to produce renewable fuels and valuable chemicals [1]. Biomass feedstocks are classified into three general categories: lignocellulosic (e.g., bagasse, corn stover, wood, etc.), amorphous sugars (e.g., starch, glucose, etc.), and triglycerides (e.g., vegetable oil) [2]. Lignocellulosic biomass is the most abundant, cheapest, and fastest annually grown, and thus is a desirable feedstock. Lignocellulosic biomass has not yet become economically and efficiently feasible for conversion into liquid and chemicals to meet future chemical and energy needs; it requires further development of conversion processes. The U.S. Department of Energy has identified the top 10 biorenewable compounds with potential to constitute primary building blocks in our future energy and chemical landscape [3]. Extensive research has been carried out with the goal of developing techniques for efficient conversion of biomass into a broad spectrum of products.

Biomass conversion processes can be broken down into thermochemical, biological, and catalytic conversions. Methods that use chemical (primarily heterogeneous catalysts) are well recognized in both the petroleum and the chemical industries. Traditionally, catalytic systems are categorized as homogeneous, heterogeneous, and enzymatic. Homogeneous catalysis occurs when the catalyst is in the same phase as the reactant (liquid or gas), and
heterogeneous catalysis occurs when the catalyst is in a separate phase from the reactants. Enzymatic catalysis is a subset of homogeneous catalysis occurring in biological units [4]. Heterogeneous catalysis has advantages over homogenous catalysis because it typically occurs in a solid phase and can therefore be easily separated and recycled from liquid and/or gas reactants and products. Furthermore, heterogeneous catalysts are non-corrosive, stable, and durable under standard reaction conditions. Conventional catalytic conversion processes require high temperatures (above 100°C), high pressures (> 10 bar), and precious metals (Pt, Pd, Ru) [5]. Electrocatalytic conversion has an advantage over conventional catalytic conversion because it is feasible at ambient temperature and atmospheric pressure, and uses base metals (in some cases) along with precious metals. In addition, it permits reaction rate and product selectivity to be precisely controlled by applying potential in electrocatalytic conversion systems, while it is difficult to precisely control reaction rate and product selectivity in catalysis systems [6].

There is increasing importance of electrochemical catalytic processes, particularly for clean energy production and conversion. Recent progress has also encouraged research groups to revisit electrochemistry for other sustainable conversions, and in particular to revisit electrosynthesis/electroorganic synthesis for production of bio-based chemicals. Electrocatalysis has emerged as a promising approach for converting bio-based chemicals to value-added products. Two classes of reactions have received significant attention: hydrogenation and oxidation. While electrocatalysis is still an emerging field, the recent increase in published articles on this topic and the variety of systems studied (various metals, various reaction conditions, many reactants) calls for a broader reflection on potential
opportunities for these technologies and examining conventional heterogeneous catalysis, current challenges, gaps in knowledge, and future opportunities.

Electrocatalytic processes are directly related to electrical energy generation and storage and can potentially be used to process biomass feedstocks with higher efficiency. Furthermore, electrochemical potential applied at the aqueous/metal interface can, in contrast to chemical catalytic reactions, result in significant changes in reaction kinetics, mechanisms, and pathways. Electrocatalysis is an emerging technology for biomass conversion, because electrocatalysis is anticipated to play an increasingly more critical role in sustainable energy. This review discusses the status and challenges of electrocatalytic oxidation of bio-based glycerol compound that have primary targeted common functionalities: hydroxyl. Important reaction parameters, including electrode catalysts, electrode potential, electrolyte, reaction mechanisms, along with their thermodynamics, are reviewed. Current challenges and future opportunities are also discussed.

2.3 Electrocatalytic oxidation of alcohols

The general underlying mechanism of electrocatalytic oxidation is not yet fully developed. From a general point of view, electrooxidation of short chain aliphatic alcohols requires the presence of an expensive Pt precious metal under ambient pressure and temperature along with an acidic media. However, it is well known that Pt is readily poisoned by CO like an intermediate species formed during methanol oxidation at low temperature. It has been found that Pt-based binary or ternary catalysts, Pt-M₁, Pt-M₁-M₂, (M= Ru, Sn, Rh etc) can improve the reaction kinetics of methanol electrooxidation based on a bifunctional effect through a mechanism promoted by the second metal and/or by tuned electronic
properties of Pt via an intrinsic mechanism [7-11]. The bifunctional effect can be shown using the following equations [12]:

\[
\begin{align*}
\text{Pt} + \text{CH}_3\text{OH} & \rightarrow \text{Pt-(CH}_3\text{OH)}_{\text{ads}} \quad (1) \\
\text{Pt-(CH}_3\text{OH)}_{\text{ads}} & \rightarrow \text{Pt-(CO)}_{\text{ads}} + 4\text{H}^+ + 4\text{e}^- \quad (2) \\
\text{M} + \text{H}_2\text{O} & \rightarrow \text{M-(H}_2\text{O)}_{\text{ads}} \quad (3) \\
\text{M-(H}_2\text{O)}_{\text{ads}} & \rightarrow \text{M-(OH)}_{\text{ads}} + \text{H}^+ + \text{e}^- \quad (4) \\
\text{Pt-(CO)}_{\text{ads}} + \text{M-(OH)}_{\text{ads}} & \rightarrow \text{Pt} + \text{M} + \text{CO}_2 + \text{H}^+ + \text{e}^- \quad (5)
\end{align*}
\]

According to Equations 1 and 2, after methanol adsorption on the Pt catalyst, dehydrogenation (C-H bond cleavage or C-H activation) of methanol proceeds to produce CO\(_{\text{ads}}\). Equations 3 and 4 illustrate water activation on M. Based on Equation 5, Pt and M further cooperate to oxidize CO\(_{\text{ads}}\) to yield CO\(_2\). Neurock’s group has used a single crystal model catalyst strict with DFT simulation to calculate energetics for the CH\(_3\)OH dehydration steps to further elucidate that methanol dehydration proceeds via the reaction path shown in equation 6 [13]:

\[
\begin{align*}
\text{CH}_3\text{OH}_{\text{ads}} & \rightarrow \text{CH}_2\text{OH}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{CHOH}_{\text{ads}} + 2 \text{H}_{\text{ads}} \rightarrow \text{COH}_{\text{ads}} + 3 \text{H}_{\text{ads}} \rightarrow \text{CO}_{\text{ads}} + 4 \text{H}_{\text{ads}} \quad (6)
\end{align*}
\]

Current understanding of detailed mechanisms of electro-oxidation of alcohol remains very limited, and need to be advanced to achieve more efficient oxidation performance.

2.3.1 Glycerol: a model polyol compound

Glycerol is a non-toxic, non-flammable, and non-volatile biorenewable alcohol fuel obtained as a byproduct of the transesterification reaction that occurs in the production of biodiesel so, as a result, glycerol can today be obtained at relatively lower market prices [14]. From a practical application point of view, glycerol has great potential to constitute
one of the primary building blocks for future production of valuable chemicals for use in polymers, foods, cosmetics, detergents, and pharmaceuticals [15], as shown in Fig 1. Glycerol has three hydroxyl (OH) groups attached to each carbon atom. It can serve as a starting point for production of a series of high value oxygenated chemicals, e.g., glyceric acid, tartronic acid, mesoxalic acid, and glycolic acid, by adding the correct amount of oxygen and breaking the C-C glycerol bond [16, 17]. Such high-value oxygenated chemicals have the potential to be further upgraded into fuel additives or high-density fuels. Traditional production of these oxygenated compounds is costly, not environmentally friendly when produced through stoichiometric oxidation using strong acids [18, 19], or exhibits slow fermentation processes accompanied by low output yields.

From a fundamental catalysis science point of view, glycerol is an ideal polyol for studying reaction mechanisms because it has three hydroxyl (OH) groups attached to each of its carbon atoms. It has both primary and second hydroxyl groups and contains two C-C bonds, making it easier to be broken compared to C₂ ethylene glycol. Study of selective oxidation of glycerol to targeted product requires a more thorough understanding of oxidation pathways, for example, in how to oxidize glycerol to tartronic acid with high yield, and oxidation of two primary OH but not a secondary OH while maintaining 2 C-C bonds.

In the past, several research studies have broadly investigated heterogeneous catalytic oxidation of glycerol using noble-metal catalyst (Pt, Pd, Ru) in acidic media under relatively high temperature (above 100°C). In recent decades, a significant number of fundamental investigations have been carried out on electrocatalytic oxidation of small organic molecules as a promising green route replacement [20-26]. Electrocatalytic oxidation of glycerol has obvious advantages over other oxidation routes for glycerol
transformation, including 1) practical selective oxidation is an aqueous-phase catalytic system under moderate conditions (e.g., 20-80°C, 3-10 bar), 2) electrode potential that can be used to regulate reaction pathway, thus selectively producing desired oxidation products, 3) cogeneration of electrical energy in a fuel cell-like electrochemical reactor, 4) In basic electrolyte, Au can be used as an electrocatalysts to produce well-controlled product selectivity, and 5) it can be considered a very attractive green process due to its low environment impact [27-29], especially when compared to current stoichiometric oxidation processes. However, controlled partial (selective) electrocatalytic oxidation remains a challenge in heterogeneous catalysis [30], the catalyst selectivity is unsatisfactory with Pt, Pd, Au precious metals. This difficulty is mainly due to a lack of deep understanding of mechanistic oxidation steps, thus rational design of more efficient oxidation catalyst is not viable. The mechanism of electrocatalytic oxidation of glycerol has been studied a great deal, as further discussed in section 2.3.6. The effect of reaction conditions such as pH, temperature, and catalyst effects has been widely investigated.

2.3.2 Thermodynamics

Table 2.1 shows the thermodynamic properties for electro-oxidation of glycerol that can be divided into either complete oxidation or partial/selective oxidation of glycerol. For example, tartronic acid has been identified as a high value fine chemical that can be used in the pharmaceutical field for treatment of osteoporosis, obesity and other derivatives in medical applications. However, its application is limited to high value-added fields because of the high cost of tartronic acid (1564 US$/g) [31]. The thermodynamic efficiency (η) and reversible potential (E₀) for partial oxidation of glycerol into tartronic acid are 98.4% and 1.170 V, respectively, comparable to those for the complete oxidation of glycerol into CO₂,
i.e., 98.4% and 1.230 V. The volumetric energy density ($W_e$) and the faradic efficiency ($\eta_e$) for the partial oxidation of glycerol into tartronic acid are 3.6 kWh L$^{-1}$ and 57.1 %, comparable to those for complete oxidation of glycerol into CO$_2$, i.e., 6.3 kWh L$^{-1}$ and 100%.

The volumetric energy density ($W_e$) and the faradic efficiency ($\eta_e$) for the partial oxidation of glycerol into higher-valued oxygenated chemicals are also reasonably comparable to those with complete oxidation of glycerol into CO$_2$. Similarly, $\eta$, $E_0$, $W_e$, and $\eta_e$ for other valuable oxygenated chemicals (e.g., mesoxalic acid and glyceric acid) are reasonably comparable to those for complete oxidation of glycerol into CO$_2$. Based on thermodynamic data, it is both theoretically feasible and practical to simultaneously generate higher-valued oxygenated chemicals and electricity from electro-oxidation of glycerol. In addition, the production of these higher-valued oxygenated chemicals will not inevitably sacrifice potential electricity generation efficiency, since the thermodynamic properties for partial oxidation of glycerol (e.g., tartronic acid, mesoxalic acid, glyceric acid) are competitive with complete oxidation of glycerol reaction (CO$_2$).

Table 2.1 Thermodynamic data of the electro-oxidation of bio renewable alcohols into target products [32].

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Final Product</th>
<th>$N_e$ [a]</th>
<th>$E_0$ [b] [V]</th>
<th>$W_e$ [c] [kWh L$^{-1}$]</th>
<th>$\eta_e$ [d] [%]</th>
<th>$\eta$ [e] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>CO$_2$</td>
<td>14</td>
<td>1.230</td>
<td>6.3</td>
<td>100</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>glyceric acid</td>
<td>4</td>
<td>1.140</td>
<td>1.8</td>
<td>28.6</td>
<td>91.1</td>
</tr>
<tr>
<td></td>
<td>tartronic acid</td>
<td>8</td>
<td>1.170</td>
<td>3.6</td>
<td>57.1</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>mesoxalic acid</td>
<td>10</td>
<td>1.117</td>
<td>4.5</td>
<td>71.4</td>
<td>98.1</td>
</tr>
</tbody>
</table>

[a] $N_e$: number of transferred electrons; [b] $E_0$: thermodynamic reversible potential; [c] $W_e$: volumetric energy density, liquid H$_2$; [d] $\eta_e$: Faradic efficiency; [e] $\eta$: thermodynamic efficiency; [f] based on predicted thermodynamic data from Ref. [33] The above table is adopted from a reference [34].
2.3.3 Electrode material (electrocatalysts)

Although thermodynamic analysis shows that electrocatalytic oxidation of alcohol can be employed at the anode of a direct alcohol fuel cell, which generates electrical energy, however, sluggish oxidation kinetics and poor selectivity towards \( \text{CO}_2 \) - complete oxidation product call urgently for development of more efficient electrocatalytic oxidation catalysts. Precious metals such as Pt, Pd, Rh, and Au have been widely investigated in studies of electro oxidation of glycerol at high pH electrolyte. These precious metal nanoparticles are generally recognized to be effective active and stable catalysts in alkaline electrolytes. Combining a precious metal catalyst with other non-noble metals (e.g. Ni, Co, Fe, etc.) can produce alloys whose aim is to increase the catalytic activity, selectivity, and stability as well as reduce the catalyst cost. It has been claimed that such bimetallic catalysts are by far more active than monometallic catalysts [35]. Various other researchers have used Au [19], Pd [36], Pt [37], Pt/Bi [38] to seek to understand the role of controlling the reaction conditions, but this is not yet fully understood in the literature. Prati and co-workers [39-42] have shown that supported Au nanoparticles can very effective catalysts for chemical oxidation of alcohols. They have shown that supported gold catalyst can be effective for glycerol oxidation and, in particular, that glycerol can be oxidized to glyceric acid with 100% selectivity, depending on the catalyst preparation method used. Bianchni and co-workers[39] have compared the behavior of monometallic (Au, Pd, and Pt) and bimetallic catalysts (Au-Pd, Au-Pt) supported on carbon to study the effects of Pd and Pt on Au. They were able to show that bimetallic catalysts are more active, indicating that a synergetic effect exists between Au and M (Pd or Pt). In the case of Pt, monometallic Pt is known to be poisoned before reaching full conversion. Overall selectivity to glyceric acid increased over that of
monometallics when bimetallic Au-Pd/C catalysts were used. Catalyst size, structure, morphologies, support type (oxides or carbon material), reaction conditions (i.e., temperature, time, ratio of catalysts to glycerol) have been found to influence catalyst selectivity and further reaction mechanisms.

2.3.4 Electrode potential and current density

The reaction pathways and product distributions of electrooxidation of glycerol are found to be strongly potential-dependent. Cyclic voltammetry (CV) can be used in electrochemical studies to measure electrochemical stability and activity of the electrocatalysts. In a CV measurement, potential is ramped linearly versus time followed by a ramp reversal at a specific time. Based on CVs, Simone, et al., has shown that Pt/C exhibits a 150 mV lower onset potential and a higher peak current than either Pd or Au. The PdAu alloy (Pd$_1$Au$_1$, Pd$_3$Au$_7$) catalysts exhibited comparatively lower onset potentials, but still higher than Pt/C [43] than mono-metal Au/C and Pd/C. Pt/C tends to exhibit higher overpotential than Pd and Au metal catalysts. Zhang, et al., found a similar trend for the noble metals Pt, Pd, and Au used for electrocatalytic oxidation of glycerol [44]. Koper, et al., successfully captured the products generated on Pt and Au polycrystalline electrodes under a wide range of potentials while demonstrating that electrode potential can serve as a facile and controlled driven force of the molecule. From one perspective regarding electrocatalysts, one would expect electrocatalysts to exhibit glycerol oxidation at lower potentials due to improved kinetics, but from another perspective, the higher current could be described as an improvement in electrocatalytic properties. The onset of oxidation does not necessarily determine the actual current that could be obtained from electrocatalysts.
2.3.5 Electrolyte pH

Due to the good solubility of alcohol in water, electrooxidation of glycerol has been widely studied in aqueous electrolytes, and reaction pathways and product selectivities have been found to be greatly influenced by electrolyte pH acidity. The kinetics of catalyst activity with respect to glycerol oxidation are significantly improved in high pH electrolyte over those in low pH electrolyte because of enhanced ion transport and facile charge transfer in alkali [45]. Koper’s investigations on electrocatalytic oxidation of alcohols has shown that the first deprotonation step is a base catalyzed step, resulting in reactive alkoxide intermediates; the second deprotonation (to the aldehyde) depends on the ability of the electrode material (e.g. Au or Pt) to abstract Hβ[46]. Davis’s work on interface studies using selective chemical oxidation catalysis has shown that the adsorbed OH species is important to acceleration of many steps in alcohol oxidation, i.e., the activation energies of first deprotonation step in the absence of OH⁻ are 204, 116 kJ/mole on Au and Pt catalysts, respectively, while with the assistance of adsorbed OH-, the activation energies drop to 22 and 18 kJ/mole on Au and Pt catalysts [29]. This elegant work concludes that presence of OH⁻ ions would greatly reduce the activation energy of the first dehydrogenation step, thereby facilitating glycerol oxidation.

Stability of electrode materials is also higher in alkaline media compared to acidic media, but in alkaline media, aldehydes are not stable and their degradation should not be misinterpreted as resulting from the catalytic activity of electrode material. Higher temperature significantly facilitates glycerol electro-oxidation; the overpotential of the catalyst decreases as the temperature increases (i.e., from 25°C to 60°C). The current
density also increases across the whole potential range tested, indicating that better kinetics are achieved at elevated temperatures [44].

2.3.6 Proposed oxidation mechanism and current understanding gaps

In alkaline media, Pt, Pd, and Au have demonstrated distinct behaviors during glycerol electrooxidation. Various electrochemical techniques have been carried out in combination with spectroscopy [8, 20, 47], mass spectroscopy [9, 48], HPLC analysis [34, 49-51], as well as DFT theoretical calculations to study the adsorbed species and reactive intermediates on the electrode surface during oxidation, and thus to elucidate the alcohol reaction pathways. In general, the primary OH of glycerol is first oxidized to produce glyceric acid, then the secondary OH is oxidized to yield tartronic acid. Glycolic and oxalic acids are subsequently produced due to C-C bond cleavage, and formic acid and carbonate are produced via glycolic intermediates.

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![Diagram](image)

Fig. 2.1 Reaction mechanisms identified for Pt/C, Pd/C, and Au/C catalysts for glycerol oxidation reaction. Catalytic material producing information regarding a reaction product or intermediate are reported on arrows [43].
Simoes, et al., has investigated glycerol electro-oxidation mechanism via electrochemical experiments and in situ infrared (FTIR) spectroscopy measurements to determine electro-catalytic behavior of catalysts based on alloys of Pd with Au and Ni and to compare them with pure Pt. Their mechanism study revealed that, with respect to Pd based and Pt catalyst, the oxidation of glycerol may lead to three different reaction products: glycerate ions, tartronate ions and mesoxalate ions., with the mesoxalate ions representing the last oxidation step before a break of the C-C bond. The species after the C-C cleavage of glycerol oxidation were not distinguished by infrared spectra. The mechanistic hypotheses were shown in Fig. 2.1. FTIR measurements merely probe the instant adsorbates or intermediates formed during glycerol oxidation. Several researchers have preferred HPLC analysis over FTIR measurements as a promising technique for detecting the presence of any stable products in the liquid electrolyte [46, 50].

Xin, et al., further studied the reaction products of potential-controlled electrooxidation of glycerol using HPLC analysis[52] to determine the role of Au. Their work, based on HPLC analysis, detected no hydroxypyruvate, indicating that mesoxalate should be generated through the tartronate pathway, compared to previous findings (Simoes, et al.,) based on FTIR measurements on Au catalyst indicating that glycerol is first oxidized to hydroxypyruvate at 0.7 V, and may be further oxidized to mesoxalate. This work further demonstrated that mesoxalate is slowly over-oxidized to oxalate, leading to a slight increase in selectivity at a longer reaction time for oxalate. Based on these results, a strong correlation between applied potential and catalyst, and oxidation product distribution was demonstrated. As shown in Fig. 2.2, at lower applied potentials of <0.4 V, the adsorbed tartronate could also be oxidized to glyoxylate, then quickly oxidized to oxalate, so oxalate
is observed without observation of glycolate. However, in this work, the researchers did not investigate electro-oxidation of intermediates in half cells or single cells to further examine their proposed reaction pathways.

![Proposed reaction path for electro-oxidation of glycerol on Au. Bold arrows: main reactions; Normal arrows: minor reactions; Green arrows: favored at low potentials; Red arrows: favored at higher potentials [52].](image)

Recently, Benipal, et al., proposed [54] a reaction mechanism for electrocatalytic glycerol oxidation on PdAg using a HPLC analysis technique to further elucidate the reaction pathway. The proposed reaction pathway was confirmed using electrocatalytic oxidation of glycerol intermediates to elucidate the products of glycerol intermediates. As shown in Fig. 2.3, the first step is to oxidize one primary hydroxyl group in glycerol to generate glycerate, making glycerate a stable reaction intermediate during the glycerol oxidation reaction. Glycerate was then rapidly oxidized into tartronate and oxalate as confirmed through electrocatalytic oxidation of glycerate. The alcohol group of tartronate is surrounded by two carboxylic acid groups so it is reasonable to hypothesize that mesoxalate is produced through
the direct oxidation at a slow rate of the hydroxyl group in tartronate. This step was not confirmed by electrocatalytic oxidation of tartronate because there was no current generation from tartronate; oxalate containing two carboxylic acid groups is inactive based on electrochemical studies, indicating it is also a dead-end chemical because a carboxylic acid group cannot be further oxidized. The glycolate presumably resulted from the C-C bond cleavage of direct glycerol at this low applied cell voltage. Although glycolate may have formed from the adsorbed glycerate and even desorbed tartronate via C-C cleavage on Au catalyst [52], this requires higher applied potentials (>0.9). We hypothesize that lactate is generated through coupled heterogeneous catalytic and homogeneous transformation of some C₃ intermediates (likely glyceraldehyde [53]) in alkaline electrolyte; indeed, distinguishing the pathways of electrochemical oxidation and electrocatalytic oxidation is an interesting research topic we are currently pursuing.

Fig. 2.3 Proposed reaction pathway for oxidation of glycerol on PdAg/CNT in alkaline media. Note: these reaction pathways do not necessarily indicate elementary reaction steps [54].
The influence of the position of the functional group in the carbon skeleton of glycerol has received some attention because it plays a significant role in reactivity. Different catalysts influence different alcohol groups of the glycerol. For example, in the case of a Pt metal catalyst, the primary alcohols are more reactive than the secondary alcohols of the glycerol. For both primary and secondary alcohols, the removal of hydrogen from the alpha position of glycerol is the first step in dissociative adsorption, mainly at low potentials [55]. Conversely, in the case of an Au metal catalyst, the reactivity of primary alcohol is usually lower than that of secondary alcohols [34]. This is related to the inductive effect of the alcohol group present in secondary alcohols of glycerol [56].

In general terms, the main products formed during oxidation of primary and secondary alcohols corresponds to aldehydes and ketones, respectively. Further oxidation of aldehydes usually leads to carboxylic acids, depending on the potential applied at the electrode. A ketone functional group represents the highest possible oxidation level, further indicating a dead-end product, so no further mild electrooxidation occurs when only a ketone functional group is present in a compound. The influence of the position of the function group in the carbon skeleton of glycerol should be investigated to seek further understanding and gain new insights into mechanisms of complex multistep electrode reactions.

It worthwhile to mention that DFT was first integrated into an experimental study to investigate the selective oxidation of a simple polyol-1,2-propanediol (PDO) to pyruvate or lactate in electrochemical reactors over carbon supported Pt and Au anode catalysts. It was found that Pt/C was highly selective for primary alcohol group oxidation to lactate (86.8%) under fuel cell conditions, but that Au/C yielded significant amounts of pyruvate, a product that has previously eluded heterogeneous catalytic studies regarding Au. Sequential
oxidation of lactate to pyruvate was not observed on Au/C but did occur slowly on Pt/C. Based on observed product distributions and linear sweep voltammetry of intermediate products, the authors proposed that the intermediates hydroxyacetone and pyruvaldehyde, not stable in high pH electrolyte, can be further oxidized to pyruvate on Au/C only if they are trapped within the thick liquid diffusion layer of the carbon cloth supported catalyst layer. Density functional theory (DFT) calculations of reaction energies identified the most favorable reaction intermediates and provided insight into the likely reaction pathways [57].

2.4 Conclusions and future directions

Electrocatalysis is a green methodology playing important role in sustainable biomass conversion and biofuel production. Electrocatalytic oxidation process is preferred over the catalytic oxidation in kinetics, reaction pathway and mechanism, as electrode potential, electrocatalysts and reaction conditions can be integrated to more accurately regulate reaction pathway and achieved high selectivity to desirable products. Further, electrocatalysis can cogenerate electricity and cogenerate valuable chemicals via fuel cell devices. Currently, the mechanistic study of electrocatalytic oxidation of polyols remains very preliminary. Integrated experimental and theoretical DFT methods have been only applied to study electro-oxidation of small molecules (e.g. formic acid, methanol or ethanol) using either single crystal model catalysts or bulk polycrystalline metal electrodes. More advanced computational methods and accurate synthesis of nano-catalysts with well-controlled size, structure need to be developed and coupled with in-situ / operando spectroscopy techniques to advance understanding of detailed pathways of electro-oxidation of longer carbon chain polyols. Moreover, there is not enough of information in terms of fundamental studies on real-world electrocatalyst particle size, catalyst structure features (e.g., step edges and kinks) and morphology on their electrocatalytic functions (activity, selectivity
and durability) which needs more investigation. One of the main opportunities of electrocatalysis is to produce cost effective large scale commodity chemicals which are not commercially available or are difficult to process. From the techno-economic point of view, designing efficient electrocatalytic reactors by coupling electro-oxidation of bio-based compounds at anode compartment with an electrochemical reduction/hydrogenation of other biomass compounds in a single flow cell reactor holds promise to improve the energy and faradaic efficiencies, and make electrochemical reactors feasible for wide-spread applications.

2.5 References


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CHAPTER 3 CARBON NANOTUBE SUPPORTED PDAG NANOPARTICLES FOR ELECTROCATALYTIC OXIDATION OF GLYCEROL IN ANION EXCHANGE MEMBRANE FUEL CELLS

Graphical abstract for “Carbon nanotube supported PdAg nanoparticles for electrocatalytic oxidation of glycerol in anion exchange membrane fuel cells” published as a TOC in Applied Catalysis B: Environmental journal.

*The material contained in this chapter is published in Applied Catalysis B: Environmental Journal, March 2017, “Carbon Nanotube Supported PdAg Nanoparticles for Electrocatalysis Oxidation of Glycerol in Anion Exchange Membrane Fuel Cells, by Neeva Benipal, Ji Qi, Qi Liu, Wenzhen Li
3.1 Abstract

Electro-oxidation of alcohol is the key reaction occurring at the anode of a direct alcohol fuel cell (DAFC), in which both reaction kinetics (rate) and selectivity (to deep oxidation products) need improvement to obtain higher power density and fuel utilization for a more efficient DAFC. We recently found that a PdAg bimetallic nanoparticle catalyst is more efficient than Pd for alcohol oxidation: Pd can facilitate deprotonation of alcohol in a base electrolyte, while Ag can promote intermediate aldehyde oxidation and cleavage of C-C bond of C$_3$ species to C$_2$ species. Therefore, a combination of the two active sites (Pd and Ag) with two different functions, can simultaneously improve the reaction rates and deeper oxidation products of alcohols (Applied Catalysis B, 2016, 199, 494). In this continuing work, Pd, Ag mono, and bimetallic nanoparticles supported on carbon nanotubes (Ag/CNT, Pd/CNT, Pd$_1$Ag$_1$/CNT, and Pd$_1$Ag$_3$/CNT) were prepared using an aqueous-phase reduction method; they served as working catalysts for studying electrocatalytic oxidation of glycerol in an anion-exchange membrane-based direct glycerol fuel cell. Combined XRD, TEM, and HAADF-STEM analyses performed to fully characterize as-prepared catalysts suggested that they have small particle sizes: 2.0 nm for Pd/CNT, 2.3 nm for PdAg/CNT, 2.4 nm for PdAg$_3$/CNT, and 13.9 nm for Ag/CNT. XPS further shows that alloying with Ag results in more metal state Pd presented on the surface, and this may be related to their higher direct glycerol fuel cell (DGFC) performances. Single DGFC performance and product analysis results show that PdAg bimetallic nanoparticles can not only improve the glycerol reaction rate so that higher power output can be achieved, but also facilitate deep oxidation of glycerol so that a higher faradaic efficiency and fuel utilization can be achieved along with optimal reaction conditions (increased base-to-fuel ratio). Half-cell electrocatalytic activity
measurement and single fuel cell product analysis of different glycerol oxidation intermediates, including C$_3$: glycerate, tartronate, mesoxalate, and lactate; C$_2$: glycolate and oxalate, over PdAg/CNT catalyst was further conducted and produced deeper insight into the synergistic effects and reaction pathways of bimetallic PdAg catalysts in glycerol electrocatalytic oxidation.

3.2 Introduction

Rapid depletion of fossil fuels makes it necessary to seek replacement of petroleum-based energy sources to lead to a sustainable future [1]. Clean and renewable energy sources are increasingly being used to replace fossil fuels, to end the progression of climate change, and to reduce pollution [2]. Prominent energy devices such as internal combustion engines have low efficiency (<13%) while emitting many harmful pollutants and greenhouse gasses [3]. Glycerol is a non-toxic, non-flammable, and non-volatile biorenewable alcohol fuel obtained as a byproduct of the transesterification reaction that occurs in the production of biodiesel [4-6]; as a result, glycerol can today be obtained at relatively lower market prices compared to other alcohol fuels (see Table 3.1). Glycerol can serve as a starting point for production of a series of high-value oxygenated chemicals such as glyceric acid, tartronic acid, mesoxalic acid, and glycolic acid, etc. [7-11]. Traditional production of these oxygenate compounds is costly, environmentally unfriendly because of stoichiometric oxidation using strong acids [12], or exhibits slow fermentation processes accompanied by low output yields [13]. A glycerol oxidation reaction (GOR) produces negative Gibbs free energy, so it can be used as a fuel fed at the anode for fuel cells to simultaneously generate electrical power and produce valuable chemicals.
Fuel cells, batteries, and electrochemical capacitors are systems considered for alternative energy/power sources. The main disadvantage of rechargeable batteries (mostly lithium-based, e.g., lithium or lithium polymer) is limited energy density [14, 15]. Fuel cell technology, a thrust research area, is an appropriate substitute to rechargeable battery technology due because fuel cells, especially direct alcohol fuel cells (DAFCs), have been recognized as green energy generators capable of converting renewable sources into electrical power [16]. To meet the world’s demand for energy, DAFCs represent a potentially promising alternative energy source to the use of fossil fuels [17, 18]. The thermodynamic efficiency of a DAFC is greater than 90% because energy from the fuel is directly transformed into electrical energy without the constraints of Carnot’s theorem [19, 20]. Anion-exchange membrane-direct alcohol fuel cells (AEM-DAFCs) have the great advantage that the kinetics of both anode and cathode reactions can be greatly enhanced by the better mass transfer and lower adsorption of spectator-charged species [17, 18, 21-24]. The byproducts associated from AEM-DAFCs also appear to produce no negative environmental impact. To more completely explore such alternative fuels, numerous studies have been carried out based on AEMFC platforms using various biorenewable fuels.

The typical performances of DAFCs are shown in Table 1. Low-temperature AEMFCs have exhibited significant advantages over other types of fuel cells because charge and ion transfer along with alcohol oxidation kinetics can be greatly improved in alkaline media. We have demonstrated a surprisingly high performance of 268.5 mW/cm² (ambient O₂, with a low Pt loading of 0.5 mg/cm², 80°C) using an AEMFC directly fed with 88 wt.% soybean biodiesel crude glycerol (one of the cheapest alcohols on the market), with the faradaic efficiency reaching 47% (6.5e⁻/14e⁻) [25]. In general, a PEM-direct ethanol fuel
cell has a peak power density (e.g., < 80 mW/cm²) and low faradaic efficiency of <30% because its dominant byproduct is acetate (4e⁻/12e⁻). SOFCs must operate at high temperatures (i.e. >750°C) and thus have relatively limited applications for portable electronics. Current biofuel cells employ enzymatic catalysts to achieve complete oxidation of alcohols, but their low output power density (< 1.0 mW/cm²), heavy dependence on the organic-living environment, and short lifetime limit biofuel cell applications to environmental remediation rather than mobile power source application. To achieve long life-time DGFCs operation, however, more robust and cheaper catalysts must be developed.

Table 3.1 The state-of-the-art of oxygen-based direct alcohol fuel cells.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fuel cost (US$/gallon)</th>
<th>Catalyst cost (mgPt/cm² MEA)</th>
<th>AEMFC (mW/cm²)</th>
<th>PEMFC (mW/cm²)</th>
<th>SOFC (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude glycerol</td>
<td>0.75-0.9</td>
<td>0.5</td>
<td>269† [25]</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Refined glycerol</td>
<td>4.0-4.8</td>
<td>0.5</td>
<td>285† [25]</td>
<td>--</td>
<td>327‡ [26]</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.3</td>
<td>&gt;10</td>
<td>168 [27]</td>
<td>246 [28]</td>
<td>1600‡ [29]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.2</td>
<td>&gt;5</td>
<td>185 [30]</td>
<td>80 [31]</td>
<td>800‡ [32]</td>
</tr>
</tbody>
</table>

†: Li group previous results, ‡: > 750°C operation. AEM: anion exchange membrane, PEM: proton exchange membrane, SO: solid oxide, FC: fuel cell, MEA: membrane electrode assembly.

Platinum (Pt) and Pt-based catalysts for DAFCs have been identified as the best electro-catalysts with respect to electrooxidation of alcohols at relatively low temperatures, where they exhibited high power density and fuel utilization efficiency [25, 33-37]. Pt can be more easily contaminated than other precious metals, limiting its stability and activity, and the high cost due to scarcity of Pt is also problematic, so extensive efforts are being carried out to rationally design new catalysts for DAFCs. Much research regarding selective oxidation of glycerol through environmentally-friendly and fast heterogeneous catalysis using monometallic/bimetallic Pd based catalysts has been conducted [7, 12, 38-41]. Since Pd is much more abundant in nature and half the cost of Pt, it is a suitable replacement of Pt.
for oxidation of a large variety of organic molecules in alkaline environments. The addition of a second metal to create Pd-M alloy catalysts has been extensively explored [42-50]. For a C₂₄ alcohol, there is a need to rationally design Pd-M catalysts to not only improve the oxidation kinetics (activity), but also to manipulate the reaction pathway to cleave a C-C bond of alcohol. Ag has up to now been much less studied in heterogeneous oxidation catalysis, even though its addition to Pd can significantly reduce the cost of the anode catalyst and may even further improve the alcohol oxidation rate. We recently designed an efficient PdAg/CNT catalyst that demonstrated better performance than Pd/CNT for alcohol (methanol, ethanol, ethylene glycol, and glycerol) oxidation in AEM-DAFCs [51]. We found that Pd can facilitate deprotonation of alcohol in a base electrolyte, while Ag can promote intermediate aldehyde oxidation and cleavage of C-C bonds of C₃ species to C₂ species, so a combination of two active sites (Pd and Ag), with two different functions, can simultaneously improve both the reaction rate and the deeper oxidation products. Previous work focused on the PdAg/CNT catalyzed alcohol oxidation reaction facilitated by Ag catalyzed aldehyde oxidation, a more general catalytic mechanism.

In the present work, we focus on a more detailed analysis of glycerol oxidation over PdAg/CNT as well as a more comprehensive physical characterization of PdAg/CNT. Full characterizations such as XRD, TEM, XPS, ICP-MS, and HAADF-STEM, were used to characterize the particle size, size distribution, structure, surface chemical state and bulk metal composition of these catalysts. The catalytic activities of catalysts toward glycerol oxidation were first compared in half-cells, and then applied as electrocatalysts for oxidation of glycerol in AEM-DAFCs to determine the product distribution. Electrocatalytic activities of different reaction intermediates (C₃ chemicals: glycerate, tartronate, mesoxalate, lactate;
C₂ chemicals: glycolate, oxalate) corresponding to these catalysts were determined to investigate the reaction pathways, with combined product distribution results obtained in single DGFCs. This study demonstrates the benefit of using an alloyed Pd-Ag bimetallic catalyst to improve peak power density and facilitate deeper oxidation products, thereby improving fuel cell performance.

3.3 Experimental
3.3.1 Chemicals

Carboxyl-group functionalized short multi-wall carbon nanotubes (8-15 nm outer diameter, 0.5-2 µm length) were purchased from Cheaptubes, Inc. Palladium (II) nitrate dihydrate (40%), silver nitrate (99%), 1-propanol (99.5%), potassium hydroxide (85%), potassium sulfate (99%), sodium borohydride (99%), sodium citrate dihydrate (99%), polytetrafluoroethylene (PTFE) ionomer solution (60%), glycerol (99.5%), lactic acid (98%), D-glyceric acid calcium salt dihydrate (99%), sodium mesoxalate monohydrate (98%), tartronic acid (97%), glycolic acid (99%), and oxalic acid (99%) were obtained from Sigma-Aldrich. The cathode Acta 4020 catalyst (Fe-based) was bought from Acta, Inc. All chemicals were used as received without further purification.

3.3.2 Catalyst synthesis and physical characterizations

Carbon-nanotube (CNT) supported nanoparticles Pd/CNT, PdAg/CNT, PdAg₃/CNT, and Ag/CNT catalysts (20 wt%) were synthesized using a modified aqueous-phase reduction method recently developed by our group [25, 51-53]. The prepared catalysts were characterized using transmission electron microscopy (TEM, JEOL 2010) with an operating voltage of 200 kV. X-ray diffraction (XRD) patterns were collected from a Scintag XDS-2000 θ/θ diffractometer using Cu Kα radiation (λ = 1.5406 Å), with a tube current of 35 mA.
and a tube voltage of 45 kV. The mean crystallite size of catalysts was calculated using the (220) peak based on a combination of Bragg’s law and the relationship between lattice and crystal-lattice spacing given by

\[
L = \frac{0.9\lambda_{K\alpha}}{B_2\theta\cos\theta_{\text{max}}}
\]

where L is the mean crystallite size, \(\lambda_{K\alpha}\) is the X-ray wavelength (1.5406 Å), B is the full width of the peak (rad) at half-maximum (FWHM), and \(\theta_{\text{max}}\) is the Bragg angle (rad) of the (220) peak position. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Amicus/ESCA 3400 with Mg K\(\alpha\) X-rays (1253.6 eV). During XPS analysis samples were not sputtered. All spectra were calibrated with a measured C 1s peak at 284.6 eV. High-angle annular dark field images were obtained using aberration-corrected scanning transmission electron microscopy (HAADF-STEM) on a Titan Themis electron microscope at 300 KV with a super-X EDS detector.

3.3.3 Electrocatalytic oxidation of glycerol and reaction intermediates in a three-electrode cell

Cyclic voltammetry was performed in a single compartment three-electrode setup (AFCELLL3, Pine Instrument), consisting of a glassy carbon working electrode (AFE3T050GC, Pine Instrument), a coiled platinum counter electrode (AFCTR1, Pine Instrument) isolated by a fritted glass tube from the main test electrolyte, a Hg/HgO reference electrode (MMO, CHI152, CH Instruments), with a 0.1 M KOH filling solution. The potential was applied with a multi-channel potentiostat (Biological). All tests were prepared and performed at ambient temperature and all potentials in the study were referred to MMO (1.0 M KOH, 0.098 V vs. SHE). The prepared catalyst’s ink was dispersed by
ultrasonication in 1-propanol to form a uniform ink (0.5 mg mL\(^{-1}\)). A glassy carbon electrode (GCE) was refined with an alumina micropolish solution and grinding paper to avoid contamination by metal particles. The working electrode was prepared by drop-casting 10 µL of ink for Pd/CNT and Ag/CNT, 20 µL of ink for PdAg/CNT, and 40 µL of ink for PdAg\(_3\)/CNT with a micro-syringe onto a polished and cleaned GCE with a working area of 0.1963 cm\(^2\). 10 µL of 0.05 wt% AS-4 anion conductive ionomer solution (Tokuyama, Inc) was added on top to affix and bind the catalyst particles. The electrolytes were composed of 1.0 M KOH + 0.1 M glycerol, mesoxalic acid, glyceric acid, tartronic acid, oxalic acid, lactic acid, or glycolic acid in deionized water. Prior to testing, all electrolytes were de-aerated by purging with high purity N\(_2\) for 30 min at ambient temperature. Ten cyclic voltammograms (CVs) were recorded for each catalyst at a constant sweep rate of 50 mV\(^{-1}\) at 25°C or 60°C.

3.3.4 Electrocatalytic oxidation of glycerol in anion exchange membrane – direct glycerol fuel cells (AME-DGFCs)

The fuel cell tests were performed on a Scribner Fuel Cell System 850e (Scribner Associates, USA) using a self-constructed membrane electrode assembly (MEA), a serpentine graphite flow field plate, and a feedback temperature control loop composed of electric heating rods and a thermocouple thermometer. The membrane-electrode assembly (MEA), with an active area of 5 cm\(^2\), consisted of a solid anion-exchange membrane (A901, 10 µm) mechanically sandwiched between anode and cathode catalyst layers on carbon cloth. Self-prepared Pd/CNT, PdAg/CNT, PdAg\(_3\)/CNT, and Ag/CNT served as anode catalysts, while commercial Acta 4020 was used as the cathode catalyst. The catalyst 4020 is Acta 4020 cathode catalyst, a noble-metal-free Fe-based cathode catalyst for use in alkaline membrane fuel cells. Standard composition of this catalyst is approx. 3.5 % wt.
transition metal (Fe-based) on carbon support. The anode catalyst ink was made by dispersing the anode catalyst powder and a 10 wt% PTFE solution (catalyst: PTFE = 8:2 mass ratio) in 1-propanol by ultra-sonication in an ice-water bath for 40 min to form a uniform ink dispersion (10 mg\textsubscript{catalyst} mL\textsuperscript{-1}) sprayed onto the carbon cloth with a spray gun. The mass of the catalyst on the carbon cloth was calculated as yielding a metal loading of 0.5 mg cm\textsuperscript{-2} for both Pd/CNT and Ag/CNT, 1.0 mg cm\textsuperscript{-2} for PdAg/CNT, and 2.0 mg cm\textsuperscript{-2} for PdAg\textsubscript{3}/CNT. The cathode catalyst ink was prepared by blending the cathode catalyst powder and an AS-4 anion conductive ionomer (catalyst:AS-4 = 7:3) in 1-propanol by ultrasonication in an ice-water bath for 40 mins to form a homogenous ink dispersion that was directly sprayed on the AEM. The mass of catalyst on the AEM was calculated as providing a catalyst loading of 3.0 mg cm\textsuperscript{-2}. Additional details of fuel cell design can be found in our previous work [19, 54, 55]. The fuel was pumped through a peristaltic pump into the anode at a flow rate of 4.0 ml min\textsuperscript{-1} for performance tests and 1.0 ml min\textsuperscript{-1} for product analysis, while high-purity O\textsubscript{2} was fed into the cathode compartment at a flow rate of 0.2 L min\textsuperscript{-1} for performance tests and 0.1 L min\textsuperscript{-1} for product analysis at a backpressure of 0 psig.

3.3.5 Product analysis of glycerol oxidation in AEM-DGFC

20 mL of 4.0 M KOH + 1.0 M glycerol solution was cycled with a flow rate of 1.0 ml min\textsuperscript{-1} using a peristaltic pump between a plastic vessel and the anode chamber via a closed loop (Gilson Minipuls 3). High purity O\textsubscript{2} (>99.999%) was fed into the cathode compartment at a flow rate of 0.1 L min\textsuperscript{-1}. Electrocatalytic glycerol oxidation was performed at 60\textdegree C for 2 h at a constant voltage of 0.1 V. Product samples were periodically obtained throughout the test for analysis by high performance liquid chromatography unit (HPLC, Agilent 1100, Alltech OA-1000 column, 60\textdegree C) equipped with a refractive index detector (RID, Agilent
G1362A), and a variable wavelength detector (VWD, Agilent G1314A, 220 nm). An eluent of 5 mM aqueous sulfuric acid at a flow rate of 0.3 mL min\(^{-1}\) was applied for product separation. 20 \(\mu\)L of sample was injected into the HPLC system. All product samples were identified by comparison with standard samples. Throughout this paper, all investigated products were in their deprotonated (salt) forms in alkaline media; but for convenience of comparison with previous studies, we have reported them in acid forms. The product selectivity, glycerol conversion \((X_g)\), carbon balance, and fuel utilization \((\epsilon_f)\) were calculated using the following equations:

\[
S = \frac{\text{moles of } C_2 \text{ or } C_3 \text{ product}}{\text{total moles of } C_2 \text{ and } C_3 \text{ products}} \times 100\%
\]

\[
X_g = (1 - \frac{\text{residual moles of glycerol after reaction}}{\text{total moles of glycerol}}) \times 100\%
\]

Carbon balance = \(\sum \frac{M_{C_1} + M_{C_2} + M_{C_3} \ldots M_{C_f}}{M} \times 100\%\)

\[
\epsilon_f = \epsilon_e \times X_g
\]

where \(S\) is the selectivity of one \(C_2\) or \(C_3\) reaction intermediates; \(X_g\) is the conversion of glycerol; \(M\) is the number of moles of glycerol in the electrolyte, \(M_{C\text{C}}\) is the number of moles of carbon in each product, \(\epsilon_f\) is fuel efficiency or fuel utilization, and \(\epsilon_e\) is faraday efficiency [51].

3.4 Results and discussion
3.4.1 Physical characterization of mono and bimetallic Pd and Ag electrocatalysts

Carbon nanotube (CNT) supported monometallic Pd/CNT and Ag/CNT and bimetallic PdAg/CNT and PdAg\(_3\)/CNT were prepared using a modified aqueous-phase reduction method [51]. The morphology, particle size, size distribution, structure, surface
chemical state, and composition of the as-prepared catalysts were analyzed by X-ray diffraction (XRD), transmission electron microscopy (TEM), high-angle annular dark field via aberration-corrected scanning transmission electron microscopy (HAADF-STEM), X-ray photoelectron spectroscopy (XPS), and inductively coupled-plasma- mass spectrometry (ICP-MS). XRD patterns of all catalysts, collected at temperature ranging from 15° to 90°, exhibited typical a face-centered cubic (FCC), as shown in Fig. 3.1a. The diffraction peaks that correspond to monometallic Pd are 40°, 47°, 68°, and 81° representing the (111), (200), (220), and (311) facets, respectively. For monometallic Ag, diffraction peaks are centered at 38°, 44°, 64°, 77°, and 82°, representing the (111), (200), (220), (311), and (222) facets, respectively. The diffraction peaks of the alloyed PdAg and PdAg₃ bimetallic nanoparticles fall between those of monometallic Ag and Pd, suggesting the formation of alloy structure. No obvious phase separation is observed for either PdAg/CNT or PdAg₃/CNT. It was also noted that the XRD diffraction peaks shifted to larger angles gradually with the increase of Ag content.

The mean crystalline sizes of Ag/CNT, PdAg₃/CNT, PdAg/CNT, and Pd/CNT catalysts, calculated based on their (220) diffraction peaks using the Debye-Scherrer formula, were 13.9, 2.4, 2.3, and 2.0 nm, respectively. The TEM images of Ag/CNT, PdAg₃/CNT, PdAg/CNT, and Pd/CNT and the corresponding metal particle size histograms are shown in Fig. 3.1b-e. The average particle sizes evaluated from the TEM were 13.7, 2.4, 2.3, and 2.1 nm for Ag/CNT, PdAg₃/CNT, PdAg/CNT, and Pd/CNT, respectively, in good agreement with the results from the XRD results. The histograms of particle sizes determined from 100 randomly chosen particles in arbitrary areas showed a narrow size distribution of 10.3 to 18.0 nm for Ag/CNT, 1.9 to 3.2 nm for PdAg₃/CNT, 1.6 to 2.9 nm for PdAg/CNT,
and 1.4 to 2.8 nm for Pd/CNT. It can be observed that well-dispersed metal particles were uniformly deposited on the CNT support. The similar particle sizes and size distributions of these catalysts (Pd/CNT, PdAg/CNT, PdAg₃/CNT) provide a good platform for investigating selective electrooxidation of glycerol in alkaline electrolyte. The aqueous-phase reduction method achieved very small Pd nanoparticles under these synthesis conditions, while the Pd-Ag containing particles were slightly larger and more highly developed. Bulk metal compositions of monometallic and bimetallic catalysts were close to the set metal loading (20 wt%), indicating that Pd and Ag precursors were fully reduced during nanoparticle synthesis.
Fig. 3.1 XRD patterns of (a) Ag/CNT, PdAg₃/CNT, PdAg/CNT, and Pd/CNT catalysts. TEM images and corresponding particle size histograms of (b) Ag/CNT, (c) PdAg₃/CNT, (d) PdAg/CNT, and (e) Pd/CNT catalysts.
XPS was further used to characterize the surface oxidation states of the metals in as-prepared catalysts, and a survey XPS spectrum confirmed the coexistence of Pd, Ag, C, and O elements in as-prepared catalyst. The oxidation states of Pd and Ag were obtained by fitting the peaks of high resolution Pd 3d and Ag 3d XPS spectra, as shown in Figs. 3.2a and 2b. XPS spectra of monometallic Pd/CNT revealed both oxidized Pd²⁺ and metallic Pd⁰ chemical oxidation states (Fig. 3.2a). The addition of Ag to Pd when alloyed prevents the oxidation of Pd, so in alloyed PdAg/CNT and PdAg₃/CNT the existence of only metallic Pd⁰ in the surface oxidation state was observed. Metallic Ag⁰ was primarily present in Ag 3d of Ag/CNT, PdAg/CNT, and PdAg₃/CNT catalysts, as shown in Fig. 3.2b. Pd⁰, Pd²⁺, and Ag⁰ were detected, reflecting the efficient reduction of Pd(NO₃)₂·2H₂O and AgNO₃. A greater amount of metallic Pd⁰ in PdAg/CNT catalyst may lead to a better alcohol deprotonation effect than for monometallic Pd/CNT, resulting in higher glycerol oxidation kinetics. Furthermore, XPS were performed on as-prepared catalysts after a 2 h reaction under hard conditions of alkaline electrolyte to observe a change in the catalysts’ oxidation states (Fig. S3.1). The results showed no apparent change in the surface oxidation states of the catalysts, reflecting good stability of the catalysts. It is worth mentioning that wide XPS spectra of as-prepared catalysts after a 2 h reaction revealed the additional presence of F and Cl elements among Pd, Ag, C, and O elements that originated as impurities either from the potassium hydroxide electrolyte or from the anion-exchange membrane used in the reaction (Fig. S3.2).

HAADF-STEM elemental mapping images are shown in Fig. 3.2c and 3.2d, revealing a homogeneous distribution of Pd and Ag in a single PdAg and PdAg₃ nanoparticle along with well-developed crystalline structure; this further displays the alloy feature of PdAg/CNT and PdAg₃/CNT. The aqueous-phase reduction method achieved very small Pd
nanoparticles under these synthesis conditions, while nanoparticles containing Ag were slightly larger and more highly developed, as can be seen in the HAADF-STEM images. While it is interesting to find that nanoparticles are not exactly round-shaped, this may be due to the synthesis conditions, and details of PdAg nanoparticle growth should be further investigated in our future work.

Fig. 3.2 XPS spectra of catalysts before 2 h glycerol oxidation in AEMFC a) Pd 3d for Pd/CNT, PdAg/CNT, and PdAg$_3$/CNT, b) Ag 3d for Ag/CNT, PdAg/CNT and PdAg$_3$/CNT. HAADF-STEM-EDS mapping images of a single PdAg and PdAg$_3$ nanoparticle c) PdAg/CNT, d) PdAg$_3$/CNT.
3.4.2 Electrocatalytic oxidation of glycerol study of Pd/CNT, PdAg/CNT, PdAg₃/CNT, and Ag/CNT in half-cell

CV profiles were conducted to study electrocatalytic oxidation of glycerol over Pd/CNT, PdAg/CNT, PdAg₃/CNT, and Ag/CNT catalysts, as shown in Fig. 3.3. The results show that Pd and Ag alloyed together exhibited higher current density and lower onset potential than monometallic Pd/CNT and Ag/CNT catalysts. The onset potential of glycerol oxidation shifted more negatively with increasing Ag content -0.44 V > -0.39 V > -0.35 V for PdAg₃/CNT, PdAg/CNT, and Pd/CNT, but the current density for PdAg/CNT is higher than that for PdAg₃/CNT, indicating that further addition of Ag will diminish the current density due to blockage of Pd active sites by the additional Ag content, so the synergetic effect of PdAg/CNT improves the total reaction rate of the glycerol oxidation reaction. The Ag/CNT catalyst, however, displayed very little or no activity directed toward electrocatalytic glycerol oxidation at the same applied potential. In general, it can be concluded that Ag is relatively catalytically inactive towards alcohol oxidation within the fuel cell anode potential window (<-0.2V vs. MMO).

Fig.3.3 Cyclic Voltammograms of glycerol oxidation reaction on Pd/CNT, PdAg/CNT, PdAg₃/CNT, and Ag/CNT catalysts in 1.0 M KOH + 0.1 M glycerol, 50 mV s⁻¹, 25°C.
3.4.3 Electrocatalytic oxidation of glycerol study of Pd/CNT, PdAg/CNT, and PdAg₃/CNT in single-cell

Cell polarization and power density curves of direct glycerol AEMFC using Pd/CNT, PdAg/CNT, and PdAg₃/CNT anode catalysts are shown in Fig. 3.4. The open circuit voltage (OCV) of the direct glycerol AEMFC with PdAg/CNT was 0.83V, 0.03 V higher than that for PdAg₃/CNT and 0.07 V higher than that for Pd/CNT. The peak power density (PPD) of the direct glycerol AEMFC with PdAg/CNT was 76.5 mW cm⁻², 9.1% higher than that for PdAg₃/CNT and 29.0% higher than that for Pd/CNT. It is also interesting to observe that PdAg₃/CNT achieves a limited reaction rate in the higher current density region because of reactant mass transfer issues. The higher content of Ag causes the more active sites of the Pd catalyst to be covered by the Ag, leading to a decrease in performance. These single-cell performance results are consistent with half-cell results.

Fig.3.4 Polarization and power density curves of DGFC with anodes: (Pd/CNT, 0.5 mg cm⁻²; PdAg/CNT, 1.0 mg cm⁻²; PdAg₃/CNT, 2.0 mg cm⁻²), 2.0 M KOH + 1.0 M glycerol, 2.0 mL min⁻¹. Tokuyama A201; cathode: Fe-based catalyst (Acta 4020), 3.0 mg cm⁻²; O₂, 60°C.
3.4.4 Glycerol oxidation product distribution in AEMFCs on Pd/CNT, PdAg/CNT, and PdAg₃/CNT

We further examined glycerol oxidation products from using Pd/CNT, PdAg/CNT, and PdAg₃/CNT anode catalysts for 2 h at 60°C in AEM-DGFC at constant fuel cell voltage (0.1 V). The oxidation products were analyzed using HPLC. Table 3.2 shows the product selectivity distribution of glycerol oxidation for Pd/CNT, PdAg/CNT, and PdAg₃/CNT. It can be observed that the selectivity of C₂ species, i.e., oxalate and glycolate on Pd/CNT, PdAg/CNT, and PdAg₃/CNT, increased as the Ag content increased, indicating that Ag contributed to a deeper C-C bond cleavage. Conversely, all the C₃ species, i.e., tartronate, mesoxalate, glycerate, and lactate on Pd/CNT, PdAg/CNT, PdAg₃/CNT, decreased as the Ag content increased. The corresponding conversion of glycerol is 48.4%, 55.0%, and 43.0% for Pd/CNT, PdAg/CNT, and PdAg₃/CNT, respectively. The increase in Ag content has resulted in higher faradaic efficiencies of 58.2% for Pd/CNT, 63.1% for PdAg/CNT, and 65.7% for PdAg₃/CNT, while the fuel utilization efficiency exhibits a volcano trend as shown in Table 3.3 because since the fuel utilization efficiency has a relationship with the conversion (Fuel utilization efficiency = faradaic efficiency × conversion), a higher Ag content may block the active sites of Pd and result in a decrease in the conversion of PdAg₃/CNT, leading to the fuel utilization efficiency drop. It is also very interesting to observe that PdAg not only improves the faradaic efficiency by 8.4% (from 58.2% to 63.1%), but also enhances the peak power density by 29% (from 59.3 to 76.5 mW/cm²).
Table 3.2 Product selectivity distribution of Pd/CNT, PdAg/CNT, and PdAg₃/CNT in AEM-DGFC. Anode fuel: 4.0 M KOH + 1.0 M glycerol, 2.0 mL min⁻¹, cathode fuel: O₂, 200 sccm, ambient pressure, 60°C. The below numbers are in %.

<table>
<thead>
<tr>
<th>Oxalate</th>
<th>Glycolate</th>
<th>Tartarone</th>
<th>Mesoxalate</th>
<th>Glycerate</th>
<th>Lactate</th>
</tr>
</thead>
<tbody>
<tr>
<td>12e⁻</td>
<td>8e⁻</td>
<td>8e⁻</td>
<td>10e⁻</td>
<td>4e⁻</td>
<td>2e⁻</td>
</tr>
<tr>
<td>Pd/CNT</td>
<td>25.3</td>
<td>8.5</td>
<td>39.5</td>
<td>3.8</td>
<td>21.7</td>
</tr>
<tr>
<td>PdAg/CNT</td>
<td>35.9</td>
<td>20.9</td>
<td>26.4</td>
<td>1.5</td>
<td>14.2</td>
</tr>
<tr>
<td>PdAg₃/CNT</td>
<td>39.2</td>
<td>37.9</td>
<td>13.7</td>
<td>0</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Table 3.3 Conversion, carbon balance, average electron transfer, faraday efficiency, and fuel utilizations of DGFC on Pd/CNT, PdAg/CNT, and PdAg₃/CNT. Anode fuel: 4.0 M KOH + 1.0 M glycerol, 2.0 mL min⁻¹, cathode fuel: O₂, 200 sccm, ambient pressure, 60°C.

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>Carbon Balance (%)</th>
<th>Average Electron Transfer</th>
<th>Faraday Efficiency (%)</th>
<th>Fuel Utilization (%)</th>
<th>Power Density (mW cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/CNT</td>
<td>48.4</td>
<td>94.2</td>
<td>8.1</td>
<td>58.2</td>
<td>28.2</td>
</tr>
<tr>
<td>PdAg/CNT</td>
<td>55.0</td>
<td>89.9</td>
<td>8.8</td>
<td>63.1</td>
<td>34.7</td>
</tr>
<tr>
<td>PdAg₃/CNT</td>
<td>43.0</td>
<td>82.1</td>
<td>9.1</td>
<td>65.7</td>
<td>28.3</td>
</tr>
</tbody>
</table>

In our previous work, we reported a high pH alkaline environment (6.0 M KOH + 1.0 M glycerol), targeting a high glycerol electro-oxidation rate [51]. In the present work, we reduced the alkaline concentration from 6.0 to 4.0 M and then 2.0 M, based on considerations of environmental impact and fuel cell device material compatibility. As the KOH concentration increased from 2.0 M to 4.0 M, the glycerol conversion on PdAg/CNT jumped from 50.4% to 55.0% due to the promoted deprotonation of glycerol in a higher pH environment (Table. 3.3 and Table. S3.1). A higher KOH concentration also facilitates the oxidation of hydroxyl groups in glycerol, leading to higher selectivity of C₃ products, as shown in our previous study [51]. It can be noted that varying the KOH concentration (from 6.0 M to 2.0 M) has only minor effects on product distribution.
To further investigate the electrocatalytic oxidation of glycerate, mesoxalate, tartronate, lactate, oxalate, and glycolate over Pd/CNT, PdAg/CNT, PdAg$_3$/CNT, and Ag/CNT catalysts, CVs were conducted at 60°C, with the results shown in Fig. 3.5. The activities of the prepared catalysts for oxidation of intermediates were compared in a half-cell reactor by observing the oxidation onset potential and peak current density. The onset of glycerate oxidation (Fig. 3.5a), containing two alcohols and one carboxylic acid groups, occurred at a much lower potential (-0.47 V) on PdAg/CNT compared to that for Pd/CNT and Ag/CNT, reflecting the synergistic effect of Pd-Ag in promoting the alcohol group oxidation. Similarly, in the low potential range, the current density for PdAg/CNT was significantly higher than that for Pd/CNT and Ag/CNT catalysts within the fuel cell anode potential (-0.22 V vs. MMO). This is consistent with electro-oxidation glycolate (containing one primary alcohol and one carboxylic acid group, Fig. 3.5f) results, for which PdAg shows the lowest potential (-0.56 V). In comparison, oxalate containing two carboxylic acid groups is inactive over all four catalysts (Fig. 3.5e), indicating that it is a dead-end chemical because a carboxylic acid group cannot be further oxidized. It is interesting to note that tartronate and lactate are quite stable under the scanned potential range over the four catalysts (Fig. 3.5c and 3.5d), even though they both contain an alcohol group; this might be due to a steric effect in which the alcohol group is protected by two adjacent inert carboxylic groups or methyl group. Mesoxalate is relatively stable on a Ag catalyst without generating notable current density at <-0.22 V (Fig. 5b) in comparison to other Pd-containing catalysts, because further oxidation of C$_3$ mesoxalate will result in C-C bond cleavage; this result suggests that Ag itself does not facilitate C-C cleavage. We must clarify that Ag itself does not effectively
facilitate C-C cleavage of desorbed mesoxalate to C₂ species as much as Pd does, especially within the AEM-DAFC anode potential window (< 0.7 V vs. RHE). However, since Ag’s specific activity (0.208 mA cm⁻²Ag) towards mesoxalate is 5.5 times that of Pd (0.038 mA cm⁻²Pd) at 0.7 V vs. RHE, Ag will remarkably help PdAg/CNT to break C-C bond of mesoxalate when its particle size reduces to 2.3 nm. The higher Ag atomic ratio in the catalyst, along with the higher activity of the catalyst towards mesoxalate oxidation, produces more C-C cleavage of mesoxalate to C₂ and C₁ products. We further found that desorbed tartronate as an oxidation of intermediates in the bulk electrolyte is quite stable for all catalysts, PdAg/CNT slightly outperforms Pd/CNT with respect to current density, as shown in Fig. 3.5c. However, it is interesting to note that tartronate is more active on PdAg₃/CNT catalysts at the higher temperature of 60°C, compared to its activity at 25°C (Fig S3.3); the mechanism should be further studied. For glycolate oxidation (Fig. 3.5f), PdAg/CNT exhibits the best activity compared to the other three catalysts (Pd/CNT, Ag/CNT, and Pd₁Ag₃/CNT), and also a close onset potential but lower current density compared to glycerate oxidation. Ag shows virtually no activity for glycolate oxidation and this interesting result supports our hypothesis that adjacent inert groups (methyl or carboxylic acid) could protect an alcohol group from oxidation. Glycerate has two alcohol groups: one primary, one secondary adjacent to a carboxylic group, while glycolate has one primary alcohol group, tartronate has one middle alcohol group adjacent to two carboxylic groups, and lactate has one middle alcohol group adjacent to a methyl and a carboxylic group, so the generated current density exactly follows the trend: glycerate > glycolate > tartronate ≈ lactate.
The electrocatalytic oxidation of intermediates of glycerol over the four catalysts were further investigated by CVs at 25°C. As shown in Fig. S3.3, the onset potentials for these four catalysts moved to slightly more positive positions as the working temperature decreased to 25°C, while the current density decreased for all these catalysts across the whole applied potential range. These shifts in onset potential and peak current density, indicate that at lower temperature (25°C) kinetics are slower for electrooxidation of glycerol intermediates on four catalysts.
Fig. 3.5 Cyclic Voltammograms of Pd/CNT, PdAg/CNT, PdAg₃/CNT, and Ag/CNT for glycerol oxidation products and intermediates in 1.0 M KOH + 0.1 M (a) glycerate, (b) mesoxalate, (c) tartronate, (d) lactate, (e) oxalate, and (f) glycolate at 50 mV s⁻¹, 60°C.
To test performance of electrocatalytic activity of glycerol oxidation intermediates over PdAg/CNT in AEMFCs, all the intermediates (glycerate, tartronate, mesoxalate, lactate, glycolate, and oxalate) were fed as anode fuel. It was observed that glycerate and mesoxalate were the only two intermediates showing stable performance under the fuel cell test conditions. Tartronate, lactate, and the other C₂ intermediates glycolate and oxalate showed no current generated to produce power in AEMFCs. The DGFC with mesoxalate showed a high peak power density of 15 mW/cm², while the one with glycerate produced a value of 9 mW/cm². The trend in intermediates’ oxidation activity obtained from the single fuel cell (peak power density) is fully consistent with half-cell tests (current density), as shown in Figs. 3.5 and 3.6: mesoxalate (15 mA/cm², 15 mW/cm²) > glycerate (1.75 mA/cm², 9 mW/cm²) > glycolate (0.7 mA/cm², unstable fuel cell performance) > tartronate ≈ lactate (hardly any current generated in both half-cell and single cell).

Fig. 3.6 Polarization and power density curves of direct glycerol oxidation products (C₃) with PdAg/CNT anode catalyst at optimized operating conditions. AEM: Tokuyama A901; cathode catalyst: Fe-based catalyst (Acta 4020), 3.0 mg cm⁻²; anode fuel: 2.0 M KOH.
3.4.6 Electrocatalytic oxidation of glycerol oxidation intermediates in single cell

Electrocatalytic oxidation of mesoxalate and glycerate (product intermediates of glycerol oxidation) was further examined to elucidate the overall glycerol oxidation pathway by continuously looping 4.0 M KOH + 0.5 M mesoxalate or glycerate (20 mL) from a plastic vessel into the anode compartment of an AEMFC for 2 h at a constant fuel-cell voltage of 0.1 V on PdAg/CNT anode catalyst at 60°C. At lower fuel-cell voltage (0.1 V) glycerol oxidation conversion would be expected to react faster [19]. Oxalate and formate products were detected with selectivities of 91.8% and 8.2% at 78.7% conversion of mesoxalate. Tartronate and oxalate were detected with selectivities of 53.0% and 47.0% at 91.3% conversion of glycerate. It can be seen that oxidation of C3 product intermediates (mesoxalate and tartronate) of glycerol provides deeper oxidation and C-C bond cleavage to C2 species, i.e., oxalate.

3.4.7 Proposed reaction pathway for glycerol oxidation over PdAg/CNT

Based on the obtained half-cell and single cell activity and product distribution results, Fig. 3.7 illustrates our proposed reaction pathways for the oxidation of glycerol with main C3 and C2 oxidation products over PdAg/CNT in AEM-DGFC. The first step was to oxidize one primary hydroxyl group in glycerol to generate glycerate, making glycerate a stable reaction intermediate during the glycerol oxidation reaction. Glycerate was furthermore rapidly oxidized into C3 tartronate and C2 oxalate (a C-C cleavage product) with selectivities of 53.0% and 47.0%, respectively. This step was confirmed using electrocatalytic oxidation of glycerate in AEM-DGFC. The alcohol group of tartronate is surrounded by two carboxylic acid groups, so it is reasonable to hypothesize that mesoxalate is produced through the direct oxidation of the hydroxyl group in tartronate at a slow rate, with Pd the active site rather
than Ag (3.8% on Pd, 1.5% on PdAg, and 0 on PdAg₃, see Table. 3.2). Electrocatalytic oxidation of mesoxalate in AEM-DGFC confirmed the cleavage of C-C bond of mesoxalate to oxalate and formate as products in AEM-DGFC; this is another route to production of C₂ oxalate. Oxalate containing two carboxylic acid groups is inactive over all four catalysts (per half-cell results), indicating that it is also a dead-end chemical because a carboxylic acid group cannot be further oxidized, in good agreement with previous observations. The glycolate from the direct C-C bond cleavage of glycerol in the oxidation process was not detected over PdAg catalysts at this low applied cell voltage. Our previous work showed that glycolate can be formed from the adsorbed glycerate and even desorbed tartronate via C-C cleavage on Au catalyst, but this requires higher applied potentials (>0.9 V vs, RHE) [19, 53], further suggesting that the reaction pathways and product distributions are strongly potential dependent. We hypothesize that lactate in small amount (<2%, Table. 3.2) is generated through a coupled homogeneous transformation of some C₃ intermediates (likely glyceraldehyde) in alkaline electrolyte; indeed, distinguishing the pathways of electrochemical oxidation and electrocatalytic oxidation is an interesting research topic on which we are currently working.
Fig. 3.7 Proposed reaction pathway for oxidation of glycerol on PdAg/CNT in alkaline media. Note: these reaction pathways do not necessarily indicate elementary reaction steps.

3.5 Conclusions

Carbon nanotube (CNT) supported Pd, PdAg, PdAg₃, and Ag nanoparticles with small sizes (2.0 nm for Pd/CNT, 2.3 nm for PdAg/CNT, 2.4 nm for PdAg₃/CNT, and 13.9 nm for Ag/CNT) and narrow size distributions were synthesized through a modified aqueous-phase reduction method and served as working catalysts. XPS spectra show that by alloying with Ag, more metallic state Pd is presented on the surface. The higher performance of AEM-DGFC with PdAg anode catalyst compared to that with Pd/CNT anode catalyst suggests that PdAg can improve the glycerol reaction rate (kinetics). The oxidation product analysis demonstrates the selectivity of the C₂ species, i.e., oxalate and glycolate on Pd/CNT, PdAg/CNT, and PdAg₃/CNT increased as the Ag content increased, indicating that Ag contributed to deeper oxidation and C-C bond cleavage. Therefore, by employing bimetallic PdAg/CNT along with optimizing reaction conditions, high overall AEM-DGFC
performances (in terms of both electrical power density and fuel utilization efficiency) can be achieved. Electrocatalytic oxidation of glycerol and intermediates in an AEM-DGFC with product analysis, along with CVs of oxidation intermediates, was conducted to elucidate the electrocatalytic oxidation pathways on PdAg catalyst. We find that glycerate and mesoxalate are the two C$_3$ intermediates leading to C-C cleavage product of oxalate, while tartronate is a relatively inert chemical whose slow further oxidation generates mesoxalate, lactate is possibly produced from homogeneous transformation of C$_3$ intermediates, and glycolate is not a favorable product under lower fuel cell anode potentials. The enhancement of glycerol oxidation over PdAg bimetallic catalyst is proposed to occur through a synergistic effect of Ag’s promotion of intermediate aldehyde oxidation and C-C breakage of C$_3$ oxygenates along with a larger amount of Pd$^0$ presented on the PdAg nanoparticle surface (determined by ex-situ XPS), as supported by combining physical characterization, electrochemical activity tests and product analysis of relevant glycerol intermediates oxidation.

3.6 Acknowledgements

We acknowledge financial support from the US National Science Foundation (CBET-1159448 and 1501124), the Iowa State University startup fund and an Iowa Energy Center (IEC) Opportunity Grant. We thank Dr. Dapeng Jing of Material Analysis and Research Laboratory of ISU for XPS analysis and Zhiyuan Qi from Dr. Wenyu Huang’s group of Chemistry Department for ICP-MS analysis. The authors are grateful to Ryan F. McSweeney and Baitong Chen of Iowa State University for assistance in fuel cell experiments.
3.7 References


3.8 Supplementary Information

Fig.S. 3.1 XPS spectra of as-prepared catalysts after 2 h glycerol oxidation in AEMFC a) Ag 3d for PdAg/CNT and PdAg₃/CNT, b) Pd 3d for PdAg/CNT, Pd/CNT, and PdAg₃/CNT
Table S 3.1 Conversion, carbon balance, average electron transfer, faraday efficiency, and fuel utilizations of electrocatalytic oxidation of glycerol on Pd/CNT, PdAg/CNT, and PdAg3/CNT in AEM. Anode fuel: 2.0 M KOH + 1.0 M glycerol, 2.0 mL min\(^{-1}\), cathode fuel: O\(_2\).

<table>
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<tr>
<th></th>
<th>Conversion (%)</th>
<th>Carbon Balance (%)</th>
<th>Average Electron Transfer</th>
<th>Faraday Efficiency (%)</th>
<th>Fuel Utilization (%)</th>
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<td>PdAg3/CNT</td>
<td>42.0</td>
<td>96.8</td>
<td>8.4</td>
<td>60.4</td>
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</table>
Fig. S.3.3 Cyclic Voltammograms of Pd/CNT, PdAg/CNT, PdAg₃/CNT, and Ag/CNT for glycerol oxidation products and intermediates in 1.0 M KOH + 0.1 M (a) glycerate, (b) mesoxalate, (c) tartronate, (d) lactate, (e) oxalate, and (f) glycolate at 50 mV s⁻¹, 60°C.
CHAPTER 4 ELECTROCATALYTIC OXIDATION OF MESO-ERYTHRITOL IN ANION-EXCHANGE MEMBRANE ALKALINE FUEL CELL WITH PDAG/CNT CATALYST

Graphical abstract for “Electrocatalytic oxidation of meso-erythritol in anion exchange membrane alkaline fuel cell with PdAg/CNT catalysts” ready to be submitted as a TOC for a publication in applied catalysis B: environmental journal.

This chapter contains work that has not yet been published yet. These results need some work before its future publication.
Abstract

C-C bond cleavage during electrocatalytic oxidation of C_3+ polyols often occurs, and can significantly affect the faradaic efficiency, fuel utilization and output power density of a direct polyol fuel cell, however, it lacks deep investigation. Towards the goal of acquiring new knowledge of C-C bond breaking of polyols, herein, the electrocatalytic oxidation of a C_4 polyol meso-erythritol has been studied on carbon nanotube supported Pd- based catalyst (Pd/CNT, PdAg/CNT, and PdAg_3/CNT) in an anion-exchange membrane fuel cell (AEMFC). Our results show that PdAg/CNT improves the fuel efficiency of meso-erythritol oxidation by contributing to the C-C bond cleavage of meso-erythritol to C_3 and C_2 chemicals. Based on the analysis of electro-oxidation products and half-cell cyclic voltammetry (CV) of intermediates, a meso-erythritol electro-oxidation pathway has been proposed, which shows Ag is likely to assist Pd to promote the cleavage of C-C bonds of meso-erythritol.

Communication

There is an increasing need to explore environmentally beneficial green energy sources for rapidly growing global energy needs because of diminishing fossil fuel resources. Sustainable energy conversion and storage technologies, such as fuel cells, metal-air batteries, flow cells, etc., attract enormous attention given their potential for high energy-conversion efficiency and environmental advantages [1-5]. Electrocatalysis is anticipated to play an increasingly critical role because it is an emerging technology for use in biorenewable feedstock conversion for cogeneration of electricity and chemicals via AEMFC devices [6-9]. Anion exchange membrane fuel cells (AEMFCs) have attracted enormous attention as a potential solution for alleviating current energy issues [10-13]. In
high pH media, the reaction kinetics of alcohol oxidation at the anode and oxygen reduction reactions at the cathode are greatly improved due to facilitated charge transfer.

Polyols (e.g. glycerol, xylitol, sorbitol) have been identified by US-DOE among the top 10 biomass-derived chemicals and will serve as feedstock building blocks for future production of chemicals, fuels and polymers [14, 15]. Many research studies have been devoted to the development of highly-selective catalysts to efficiently convert glycerol to higher-valued oxygenated chemicals [8, 16-19]. In contrast to Pt and Au catalysts, Pd nanoparticles have demonstrated a unique catalytic ability in enhancing selectivities and achieving deeper C-C cleavage. The studies of electrochemical behavior of C₃ model molecule glycerol on PdAg/CNT anode catalysts in AEMFCs have been thoroughly investigated in our previous studies [20]. That work focused on PdAg/CNT catalyzed alcohol (methanol, ethanol, ethylene glycol, and glycerol) oxidation reaction facilitated by Ag-catalyzed aldehyde oxidation in a general catalytic mechanism [21]. Our more recent work has focused on a more detailed analysis of glycerol oxidation over PdAg/CNT in AEMFCs [22], has demonstrated that the selectivity of C-C bond cleavage products: the C₂ species, i.e., oxalate and glycolate on Pd/CNT, PdAg/CNT, and PdAg₃/CNT increased as the Ag content increased, indicating that Ag contributed to deeper oxidation of C-C bond cleavage.

However, deeper insights into C-C cleavage of polyols during electrochemical oxidation remain limited. This work attempts to understanding the C-C cleavage mechanisms is to investigate the simplest polyol with two kinds of C-C bonds, gaining insights into preferable C-C breaking sequence of polyols to lay a solid foundation for further study of electrocatalytic oxidation of longer carbon chain bio-polyols, such as C₅ xylitol or
C₆ sorbitol. In contrast to C₃ polyol glycerol that has two identical primary C-C bonds, C₄ polyol meso-erythritol has two primary and one secondary C-C bonds, so its study might provide us with new knowledge with respect to determining which C-C bond is preferably broken. Study of electrocatalytic oxidation of meso-erythritol in alkaline AEMFCs on Pd based has also not to the best of our knowledge been previously done.

Meso-Erythritol (1,2,3,4-butanetetrol) is a sugar polyol used as a food additive because health properties, e.g., it is low in calories, is a tooth-friendly sweetener, and is safe for diabetics because it has no impact on blood insulin or glucose levels [23, 24]. Erythritol is a naturally-occurring molecule found in fruits such as melons, grapes, pears, and in some fermented foods. It has been mass-produced at an industrial level from starch, sucrose, and glucose via enzymatic and fermentation processes [25, 26]. In addition to its possible applications in polymers, chemistry, and pharmaceuticals, meso-erythritol has also become an interesting subject for possible use in electrochemistry. Cherqaoui, et al., demonstrated that meso-erythritol provides a slow reaction with a bare polycrystalline Pt electrode in 0.1 M HClO₄ for electrocatalytic oxidation of meso-erythritol, and fourier transform infrared spectroscopy (FTIR) was used for reaction mechanisms for the oxidation of erythritol [27]. Meso-erythritol has also received some study in the electrochemistry area. Electrocatalytic studies of oxidation of meso-erythritol appear to hold great promise for future development of alkaline AEMFCs in cogeneration of higher-valued chemicals and electrical energy, and its detailed reaction pathway need to be elucidated.

In this communication, Pd, Ag mono, and bimetallic nanoparticles supported on carbon nanotubes were prepared with an aqueous-phase reduction method used for the first time to produce meso-erythritol oxidation in alkaline AEMFCs. The reaction pathways of
electrocatalytic oxidation of meso-erythritol into valuable chemicals under mild reaction conditions have been discussed in terms of half-cell and single-cell findings. The addition of Ag content into Pd catalyst, has been found to facilitate C-C bond cleavage of meso-erythritol.

Pd, Ag mono, and bimetallic nanoparticles, supported on carbon nanotubes with particle sizes: 2.0 nm for Pd/CNT, 2.3 nm for PdAg/CNT, 2.4 nm for PdAg₃/CNT, and 13.9 nm for Ag/CNT, were prepared using an aqueous-phase reduction method recently developed by our group [8, 10, 11, 21]. The prepared catalysts were comprehensively characterized via XRD, TEM, XPS, ICP-MS, and HAADF-STEM in our previous publication [22]. Cyclic Voltammetry results show that Pd and Ag, alloyed together (PdAg/CNT or PdAg₃/CNT), produced higher current density and lower onset potential than monometallic Pd/CNT and Ag/CNT catalysts, as shown in Fig.4.1. The Ag/CNT material, however, exhibited no activity toward electrocatalytic meso-erythritol oxidation at the same applied potential, leading to the conclusion that Ag is relatively catalytically inactive with respect to alcohol oxidation within fuel cell anode potential (-0.2 V vs. MMO).
Fig. 4.1 Cyclic voltammograms of Pd/CNT, PdAg/CNT, PdAg₃/CNT, and Ag/CNT for meso-erythritol oxidation in N₂ purged 1.0 M KOH + 0.1 M meso-erythritol, 50 mV s⁻¹, 25°C.

The electrocatalytic properties of Pd/CNT, PdAg/CNT, and PdAg₃/CNT anode catalysts towards meso-erythritol were then evaluated in AEMFCs under optimized conditions, as shown in Fig. 4.2. The open circuit voltage (OCV) of the direct meso-erythritol AEMFC with PdAg/CNT was 0.87 V, 0.14V higher than that for PdAg₃/CNT and 0.02 V higher than for Pd/CNT. The peak power density (PPD) of the direct meso-erythritol AEMFC with PdAg/CNT was 153.7 mW cm⁻², 17.8 % higher than that for PdAg₃/CNT and 34.5 % higher than that for Pd/CNT. The higher content of Ag in PdAg₃/CNT catalyst caused the active sites of the Pd catalyst to be covered by Ag, limiting the reaction rate in the higher current density region and decreasing performance.
Fig. 4.2 Polarization and power density curves of direct meso-erythritol fuel cell with Pd/CNT, 0.5 mg cm$^{-2}$; PdAg/CNT, 1.0 mg cm$^{-2}$; PdAg$_3$/CNT, 2.0 mg cm$^{-2}$; 6.0 M KOH + 1.0 M meso-erythritol, Tokuyama A201; Fe-based catalyst (Acta 4020), 3.0 mg cm$^{-2}$; O$_2$, 80$^\circ$C.

Further, meso-erythritol oxidation products were also examined by HPLC on Pd/CNT, PdAg/CNT, and PdAg$_3$/CNT anode catalysts for 2 h at 60$^\circ$C in AEMFC at a constant fuel cell voltage of 0.1 V. It has been demonstrated that the selectivities are highly dependent on the applied potentials [18, 28]. It has demonstrated that production of valued chemicals from polyol can be achieved with electricity cogeneration. Table 4.1 shows the product selectivity distribution of meso-erythritol oxidation; it can be observed that the selectivity of the C$_2$ species, i.e., oxalate, increased as the Ag content increased, indicating that Ag contributed to a deeper C-C bond cleavage, but the selectivity of C$_2$ species, i.e., glycolate decreased as the Ag content increased. The variation in selectivities of the C$_2$ species must be dependent on whether the C-C bond cleavage occurs on 1$^\circ$ or 2$^\circ$ carbons of
meso-erythritol, as discussed later in the description of the proposed mechanism. Conversely, all the C₃ species and C₄ species, i.e., tartrate, malate, tartronate, glycerate on Pd/CNT, PdAg/CNT, PdAg₃/CNT, decreased as the Ag content increased.

Table 4.1 Product selectivity distribution of meso-erythritol on Pd/CNT, PdAg/CNT, and PdAg₃/CNT in AEMFC. Anode fuel: 1.0 M KOH + 0.5 M meso-erythritol, 2.0 mL min⁻¹, cathode fuel: O₂, 200 sccm, ambient pressure, 60°C.

<table>
<thead>
<tr>
<th></th>
<th>Oxalate</th>
<th>Tartronate</th>
<th>Tartrate</th>
<th>Malate</th>
<th>Glycerate</th>
<th>Glycolate</th>
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<td>Pd/CNT</td>
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<td>2.7</td>
<td>4.0</td>
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<td>26.1</td>
</tr>
<tr>
<td>PdAg₃/CNT</td>
<td>47.3</td>
<td>7.9</td>
<td>1.3</td>
<td>3.0</td>
<td>19.9</td>
<td>18.2</td>
</tr>
</tbody>
</table>

The conversion of meso-erythritol in a 2 h interval was 69.4%, 66.4%, and 58.8% for Pd/CNT, PdAg/CNT, PdAg₃/CNT, respectively. The increase in Ag content resulted in higher faraday efficiencies of 43.4% for Pd/CNT, 44.5% for PdAg/CNT, and 47.1% for PdAg₃/CNT, while the fuel utilization efficiency exhibited a volcano trend, as shown in Table 4.2. A higher Ag content in a Pd catalyst (in this case Pd₁Ag₃) may block the active sites of Pd and result in a decrease in conversion of PdAg₃/CNT, leading to a drop in fuel utilization efficiency. At the same time, the carbon balance increased from 82.4% to 93.7%, indicating that fewer C₂ products (glycolate and oxalate) were oxidized into C₁ products (formate and carbonate). The addition of Ag to Pd not only improves the Faraday efficiency by 7.8%, but also enhances the peak power density by 34.6%.

Table 4.2 Conversion, carbon balance, average electron transfer, faraday efficiency, and fuel utilizations of electrocatalytic oxidation of meso-erythritol on Pd/CNT, PdAg/CNT, and PdAg₃/CNT in AEMFC.

<table>
<thead>
<tr>
<th></th>
<th>Conversion (%)</th>
<th>Carbon Balance (%)</th>
<th>Average Electron Transfer</th>
<th>Faraday Efficiency (%)</th>
<th>Fuel Utilization (%)</th>
<th>Power Density (mW cm⁻²)</th>
</tr>
</thead>
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<td>44.5</td>
<td>29.5</td>
<td>153.7</td>
</tr>
<tr>
<td>PdAg₃/CNT</td>
<td>58.8</td>
<td>93.7</td>
<td>8.5</td>
<td>47.1</td>
<td>27.7</td>
<td>126.3</td>
</tr>
</tbody>
</table>
The proposed pathway of meso-erythritol oxidation on PdAg/CNT in AEMFC based on oxidation products analysis by HPLC/NMR and CV of important intermediates is shown in Fig. 4.3. Two stable non C-C breaking C₄ products tartrate and malate have been observed. The oxidation of two primary hydroxyl groups of meso-erythritol generates tartrate. Malate has a similar molecule structure as compared with tartrate, and contains two primary carboxylic acids, one secondary alcohol group and one secondary methyl group. Malate is hypothesized to be generated through coupled heterogeneous electrocatalytic oxidation and homogeneous transformation of meso-erythritol. There is no further oxidization of tartrate and malate based on CV (Fig. S4.1a and b), suggesting they are “dead-end products” (No C-C breaking occurred on the two chemicals). Oxidation of two secondary hydroxyl groups of meso-erythritol generates 1,4-dihydroxybutane-2,3-dione with two ketone groups, which is not stable in alkaline electrolyte in nature and could further transform to other products.

On the C-C cleavage mechanism, cleaving one of primary C-C bonds (1° C-C) of an adsorbed C₄ reactive intermediate and then oxidizing the primary hydroxyl group will produce glycerate. Half-cell CV results have shown that the two C₄ chemicals tartrate and malate in the alkaline electrolyte were stable in the applied potential range. Cleavage of 1,4-dihydroxybutane-2,3-dione’s 1° C-C bond will not lead to glycerate production (instead glyceraldehyde is the product, but it is not detected). All these results indicate the three desorbed C₄ chemicals (tartrate, malate, and 1,4-dihydroxybutane-2,3-dione) are not the intermediates, but other C₄ reactive intermediates, which elude from HPLC detection, lead to 1° C-C breakage to produce glycerate.
Glycerate has shown to be a reaction intermediate during the meso-erythritol oxidation reaction on PdAg catalyst (Fig S2a), and it can be furthermore transformed into C$_3$ tartronate and C$_2$ oxalate (a C-C cleavage product) via its electrocatalytic oxidation in AEMFC as what we have previously reported [22]. In comparison, both tartronate and oxalate were observed to be “dead end products” because their functional groups were not further oxidized (no apparent current generated based on half-cell results), as shown in Fig. S2b and Fig.S3a.

Our experiments show that glycerate oxidation will not lead to glycolate production and tartronate is a “dead-end product”, indicating glycolate is not likely generated from tartronate and glycerate. We speculate that C$_2$ chemical glycolate was generated from the direct secondary C-C bond (2$^o$ C-C) cleavage of a meso-erythritol-derived C$_4$ reactive intermediate, in the oxidation process over PdAg catalyst. In our previous study [21], we have found that the C-C bond between a ketone and carboxylic group (O=C-COOH) is easy to be cleaved within the fuel cell anode potential window. Therefore, assuming a C-C bond between two ketone groups (O=C-C=O) can also be cleaved, 1,4-dihydroxybutane-2,3-dione should be one of the reactive intermediates leading to glycolate production via 2$^o$ C-C cleavage of meso-erythritol.

Glycolate in the alkaline electrolyte is known to be an unstable reaction intermediate on PdAg catalysts in the applied potential range (<0.9 V vs. RHE) based on the CVs (Fig S3b), we have found that the main product of glycolate oxidation on Pt/C catalyst at 0.6 V vs. RHE is not formate or carbonate (C-C breakage products), but oxalate [28]. Therefore, oxalate can be generated from either oxidation of glycerate’s hydroxyl group or C-C cleavage of glycerate. As outlined in the reaction pathway (Fig. 4.3), it is self-convincing
that glycolate is the only product from 2° C-C breakage of meso-erythritol (likely via the intermediate 1,4-dihydroxybutane-2,3-dione), while glycerate and tartronate are products from 1° C-C breakage of meso-erythritol (derived intermediates). However, since oxalate can be produced from either 1° C-C (oxidation of primary OH in glycolate) or 2° C-C (C-C breakage of glycerate) breakage of meso-erythritol, further study is needed to clarify the ratio of oxalate from glycolate and glycerate and examine the products from 1,4-dihydroxybutane-2,3-dione oxidation, thus, the ratio of 1° C-C cleavage and 2° C-C cleavage may be estimated. This strategy and generated knowledge can be applied to longer carbon-chain xylitol and sorbitol (C₅, C₆ polyol) electrocatalytic oxidation study.
Fig. 4.3 Proposed reaction pathway for oxidation of meso-erythritol on PdAg/CNT in alkaline media. Notes: These reaction pathways do not necessarily indicate elementary reaction steps, they are based on reaction intermediates/products examined by HPLC/NMR.

In conclusion, we have successfully demonstrated cogeneration of electricity and chemicals from electrocatalytic oxidation of meso-erythritol on carbon nanotube supported PdAg catalysts in AEMFCs. The investigation reveals a proposed reaction pathway based on PdAg/CNT in mild conditions while differentiating the C-C bond cleavage on both primary and secondary C-C bonds of meso-erythritol. It is likely that PdAg catalyst favors
C-C bond cleavage of primary C-C bonds of meso-erythritol predominately over secondary 
C-C bonds of meso-erythritol.

We acknowledge financial support from the US National Science Foundation (CBET-1159448, 1501124), the Iowa State University startup fund and an Iowa Energy Center (IEC) Opportunity Grant. We thank Machel Forrester from Dr. Eric W. Cochran Lab’s for an attempt to synthesizing 1,4-dihydroxybutane-2,3-dione due to its commercially unavailability. The authors are grateful to Baitong Chen of Iowa State University for assistance in fuel cell experiments.

References


Supplementary Information

4.1 Experimental
4.1.1 Chemicals

Palladium (II) nitrate dihydrate (40%), silver nitrate (99%), 1-propanol (99.5%), potassium hydroxide (85%), potassium sulfate (99%), sodium borohydride (99%), sodium citrate dihydrate (99%), polytetrafluoroethylene (PTFE) ionomer solution (60%), meso-erythritol (99.5%), lactic acid (98%), D-glyceric acid calcium salt dihydrate (99%), sodium mesoxalate monohydrate (98%), tartronic acid (97%), glycolic acid (99%), and oxalic acid (99%) were purchased from Sigma-Aldrich. Carboxyl-group functionalized short multi-wall carbon nanotubes (8-15 nm outer diameter, 0.5-2 µm length) were bought from Cheaptubes, Inc. The cathode Acta 4020 catalyst (Fe-based) was obtained from Acta, Inc. All chemicals were used as received without further purification.

4.1.2 Electro catalytic oxidation of meso-erythritol and intermediates in a three-electrode cell

Electrocatalytic oxidation of meso-Erythritol was conducted in a single compartment three-electrode cell setup controlled by a potentiostat (Biological), equipped with a glassy carbon working electrode, an Hg/HgO (1.0 M KOH) reference electrode and a Pt wire counter electrode. The catalyst ink was prepared by ultrasonication of catalysts in 1-propanol to form a uniform solution (0.5 mg mL\(^{-1}\)). With a micro-syringe, 10 µL of ink for Pd/CNT and Ag/CNT, 20 µL of ink for PdAg/CNT, and 40 µL of ink for PdAg\(_3\)/CNT were deposited onto a polished and cleaned glassy-carbon electrode with a working area of 0.1963 cm\(^2\). 10 µL of 0.05 wt% AS-4 anion conductive ionomer solution (Tokuyama, Inc) was added on top to bind the catalyst particles on the glassy electrode. The electrolytes were composed of 1.0 M KOH + 0.1 M meso-Erythritol, oxidative intermediates in deionized
water. Cyclic voltammetry tests (CVs) were performed at a constant sweep rate of 50 mV s\(^{-1}\) at room temperature with nitrogen bubbling.

4.1.3 Electrocatalytic oxidation of meso-erythritol in AEM-FCs

Electrocatalytic oxidation of meso-erythritol in AEM-DFC was conducted on a Scribner Fuel Cell System (850e, Fuel Cell Technology, Inc) [1-7]. Self-prepared Pd/CNT, PdAg/CNT, PdAg\(_3\)/CNT, and Ag/CNT served as anode catalysts, while commercial Acta 4020 was used as the cathode catalyst. The membrane-electrode assembly (MEA), with an active area of 5 cm\(^2\), was constructed by pressing the anode carbon cloth with anion exchange membrane, which has been sprayed with cathode catalyst. The fuel was pumped through a peristaltic pump into the anode at a flow rate of 4.0 ml min\(^{-1}\) for performance tests and 1.0 ml min\(^{-1}\) for product analysis, while high-purity O\(_2\) was fed into the cathode compartment at a flow rate of 0.2 L min\(^{-1}\) for performance tests and 0.1 L min\(^{-1}\) for product analysis at a backpressure of 0 Psig.

4.1.4 Product analysis of meso-erythritol oxidation in AEM-FCs

Electrocatalytic meso-erythritol oxidation was performed at 60\(^\circ\)C for 2 h at a constant voltage of 0.1 V. 20 mL of 1.0 M KOH + 0.5 M meso-erythritol solution was cycled with a flow rate of 1.0 ml min\(^{-1}\) using a peristaltic pump between a plastic vessel and the anode chamber via a closed loop (Gilson Minipuls 3). High purity O\(_2\) (>99.999%) was fed into the cathode compartment at a flow rate of 0.1 L min\(^{-1}\). Product samples were taken throughout the test for analysis by high performance liquid chromatography unit (HPLC, Agilent 1100, Alltech OA-1000 column, 60\(^\circ\)C) equipped with refractive index detector (RID, Agilent G1362A) and a variable wavelength detector (VWD, Agilent G1314A, 220 nm). An eluent
of 5 mM aqueous sulfuric acid at a flow rate of 0.3 mL min\(^{-1}\) was applied for product separation. 20 µL of sample was injected into the HPLC system. The products (in their deprotonated forms) were identified by comparison with authentic samples.

4.2 Supporting Figures

Fig. S. 4.1 Cyclic Voltammograms of Pd/CNT, PdAg/CNT, PdAg\(_3\)/CNT, and Ag/CNT for meso-erythritol oxidation \(C_4\) intermediates products in 1.0 M KOH + 0.1 M a) tartrate, b) malate at 50 mV s\(^{-1}\), 25°C.
Fig. S. 4.2 Cyclic Voltammograms of Pd/CNT, PdAg/CNT, PdAg₃/CNT, and Ag/CNT for meso-erythritol oxidation C₃ intermediates products in 1.0 M KOH + 0.1 M a) glycerate, b) tartronate at 50 mV s⁻¹, 25°C
Fig. S. 4.3 Cyclic Voltammograms of Pd/CNT, PdAg/CNT, PdAg₃/CNT, and Ag/CNT for meso-erythritol oxidation C₂ intermediates products in 1.0 M KOH + 0.1 M a) oxalate, b) glycolate at 50 mV s⁻¹, 25°C.
4.2.1 References


Graphical abstract for “Direct fast pyrolysis bio-oil fuel cell” published as a TOC in Fuel journal.

5.1 Abstract

Bio-oil derived from the pyrolysis of lignocellulosic biomass shows a great promise, however, needs further upgrading to potentially serve as an alternative to fossil fuels. Herein, we demonstrate that crude fast pyrolysis bio-oil can be directly used as a fuel for anion exchange membrane fuel cells (AEMFCs) to generate high power density electrical energy at low temperature (≤ 80°C). A simple aqueous-phase reduction method was used to prepare carbon nanotube (CNT) supported noble metal (Pt, Pd, Au, and Ag) nanoparticles with average particle sizes: 1.4 nm, 2.0 nm, 3.8 nm, and 12.9 nm for Pt/CNT, Pd/CNT, Au/CNT, and Ag/CNT, respectively. Direct fast pyrolysis bio-oil AEMFCs with the Pd/CNT anode catalyst and a commercial Fe-based cathode catalyst exhibit a remarkable peak power density of 42.7 mW cm\(^{-2}\) at 80°C using 30 wt% bio-oil + 6.0 M KOH electrolyte. Levoglucosan was identified as the major sugar compound with 11.1 wt% of the bio-oil composition, along with disaccharides, pyrolytic lignin, and oligomer of lignin-derived phenolic compounds. Cyclic voltammetry (CV) studies investigated the electrocatalytic oxidation of high purity levoglucosan over the four noble metal catalysts in half cell, as levoglucosan is the dominant sugar component in bio-oil. Pd/CNT, compared to other catalysts, displayed the highest activity and lowest onset potential of electrocatalytic oxidation of levoglucosan. AEMFC with high purity sugars shows ~ 1.2 to 3 times higher power density than that with fast pyrolysis bio-oil fuel.
5.2 Introduction

Currently biomass-derived fuels (biofuels) are of growing interest, mainly due to increasing concerns of global warming and environmental deterioration [1]. Consumption of fossil fuels contributes to emission of carbon dioxide (CO$_2$), nitrogen oxides (NO$_x$), and other greenhouse gases (GHG). Emission of sulfur dioxide also leads to acid rain, causing damage to crops, forests and upsetting the ecosystem equilibrium [2]. To date, over 70% of electricity has been produced by fossil fuels such as natural gas and coal, while renewable energy accounts only for only about 20% of all generated electricity [3, 4]. Clean electricity generated from renewable sources, such as solar, wind and biomass is expected to play an important role in future energy landscape, and substantial effort has been spent on research and development directed toward converting biomass into liquid fuels and commodity chemicals [5, 6], but presently they remain more expensive than their counterparts produced from fossil sources.

Fuel cells are considered as one of the most promising electrochemical energy generation devices, which can directly convert renewable resources into electrical power in an environmentally-friendly manner. Today’s fuel cells have the capability to ensure energy security, high efficiency, low operating cost, fuel versatility, and pollution-free power, largely because this electrochemical process is not limited by the Carnot theorem [7, 8]. In addition, fuel cells can be used in various scale stationary and mobile systems for quiet and continuous power generation [9]. Direct alcohol fuel cells (DAFCs) have attracted enormous attention as potential power sources, mainly because alcohol as a liquid fuel is easy to transport and convenient to store [10]. However, challenges such as poor oxidation kinetics at the anode, fuel purity requirements, and alcohol crossover limit widespread practical
applications of DAFCs technology. Recently, alkaline anion exchange membrane fuel cells (AEMFCs) are emerging quickly as a potential solution to these problems. The electrocatalytic kinetics of both anode (fuel oxidation) and cathode (oxygen reduction) are higher in an alkaline media compared to an acid media due to facile charge transfer and enhanced ion transport. Furthermore, the poison severity of impurities and contaminates on anode catalysts can be greatly alleviated in alkaline environments [11]. To explore more alternatives fuels, several studies have been carried out based on the AEMFC platform using various biorenewable fuels such as glucose [12], cellulose [13], and crude glycerol [14]. There is an urgent need to seek widely available and economical biomass-derived oil/fuels for fuel cell applications.

Bio-oil derived from fast pyrolysis of biomass is considered as a promising source of bio-based chemicals and biofuels [5, 15-18]. As traditionally recovered, bio-oil is an emulsion of water-insoluble phenolic compounds derived from lignin in an aqueous phase of water-soluble oxygenated compounds derived mostly from carbohydrate mixtures. This emulsion contains hundreds of chemicals that are difficult to separate by traditional recovery techniques such as atmospheric, fractional, steam, and vacuum distillations [1]. Pollard et al. [19] recently developed a novel bio-oil recovery method that recovers bio-oil as stage fractions with distinct chemical and physical properties using combinations of condensers with carefully-controlled coolant temperatures and electrostatic precipitators. These fractions consist of heavy ends, middle fraction, and light ends. The heavy ends can be further separated into phenolic oil and anhydrosugars, the middle fraction is mostly phenolic monomers and furans, and the light ends are an aqueous fraction containing light-oxygenated compounds such as acetic acid [20]. Fast pyrolysis bio-oil has the potential to substitute for
fossil liquid fuels after it has been upgraded by catalytic cracking, catalytic hydrogenation, or stream reforming [21]. Bio-oil contains 40% dry-weight oxygen, while petroleum-based fuels contains around 1%, so these bio-oil must be upgraded to be rightfully considered as an equivalent replacement; because highly oxygen-rich hydrocarbons bio-oil are of inferior quality for direct use as transportation fuels in combustion engines, but they may be directly served as a fuel in alkaline membrane fuel cells to generate electricity.

It should be noted that most previous AEMFC studies have been focused on high-purity fuels such as glycerol [12, 22, 23], ethanol [24], methanol [25], ethylene glycol [26], and glucose [27]. Biofuel cells with enzymatic catalysts can directly employ complex crude biomass-feedstock and waste water, but the generated power density is generally lower than 1 mW/cm², thus limiting biofuel application to environmental remediation rather than energy generation applications [28]. In the past, our group has used crude glycerol (88 wt%) [29, 30] as feedstock for AEMFCs and has shown a peak power density of 268 mW cm⁻²; this approach can be readily expanded to study more complex compound bio-oil (a mixture of over 400 compounds) as a potentially feasible fuel for AEMFCs. To the best of our knowledge, no work has yet been done on direct fast pyrolysis bio-oil for use as a fuel in AEMFCs, therefore, this study of AEMFCs directly using bio-oil establishes a generalized approach to using bio-oil to produce electrical power without the need for extensive purification of the initial raw feedstock fuel. We report a direct bio-oil AEMFC using a noble metal Pd/CNT anode catalyst to achieve a peak power density of 42.7 mW cm⁻² at 80°C. The effects of operation conditions such as the bio-oil concentration, temperature, and KOH concentration on cell performance were also studied along with the analysis of bio-oil compositions. The electrocatalytic activities of four noble metal catalysts Pd/CNT, Ag/CNT,
Au/CNT, and Pt/CNT with respect to oxidation of high purity levoglucosan (a major sugar component) were studied. The comparison of fast pyrolysis bio-oil AEMFC with high-purity sugar-fed AEMFC was investigated in both half-cell and single-cell systems.

5.3 Experimental
5.3.1 Chemicals

Palladium (II) nitrate dihydrate, silver nitrate, gold (III) chloride, polytetrafluoroethylene (PTFE), 1-propanol (99.5%), sodium borohydride (99%), sodium citrate dihydrate (99%), glucose (99%), sucrose (99%), potassium hydroxide (85%), and potassium sulfate (99%) were purchased from Sigma-Aldrich. Carboxyl-group functionalized multi-walled carbon nanotubes (8-15 nm outer diameter, 0.5-2 µm length) were procured from Cheaptubes Inc. The cathode catalyst 4020 was obtained from Acta, Inc, and levoglucosan, cellobiosan, and maltosan were received from Carbosynth. Xylose was purchased from Thermo Fisher Scientific. Stage fraction 2 bio-oil was obtained from the Iowa State University BioCentury Research Farm. All chemicals were used as received without further purification.

5.3.2 Catalyst synthesis and physical characterizations

Carbon nanotube-supported Pd, Pt, Ag, and Au nanoparticles were synthesized by an aqueous-phase reduction method [29, 31]. An aqueous-phase reduction method involves chemical reduction of dissoluble metal precursors in aqueous phase to the nucleus, controlled growth to ultimately-desired metal nanoparticles in the absence of stabilizing agents, and deposition on an appropriate carbon support. Concisely, to make Pd/CNT, Palladium (II) nitrate (105 mg) was dissolved in deionized water (1500 mL), followed by stirring at a speed of 600 rpm to ensure appropriate dispersion of the solution. Sodium citrate
dihydrate (200 mg) and sodium borohydride (40 mg) were separately dissolved in deionized water (50 mL) and then carboxyl-group functionalized multiwall carbon nanotubes (181 mg) were dispersed in 100 mL of deionized water by ultrasonication; all were then combined in a solution to reduce metal precursors and to deposit Pd nanoparticles onto the surface of the CNT. The final product Pd/CNT (20 %) was cleaned with an additional 1 L of deionized water, collected by vacuum filtration, and dried overnight in a vacuum oven. Pt/CNT, Ag/CNT, and Au/CNT were synthesized via a similar process as that used for Pd/CNT but with different metal precursors. The morphology and structure of the as-prepared catalysts were analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The TEM images were collected on a JEOL JEM-4000 FX with an accelerating voltage of 200 kV. A Scintag XDS-2000 θ/θ diffractometer (Cu Ka radiation (\( \lambda = 1.5406 \, \text{Å} \)) with 35 mA filament current and 45 kV tube voltage was used to collect XRD patterns at a continuous scan rate of 1.2 degrees per minute. The mean crystallite size of all these noble metal catalysts were calculated using the (220) peak based on the Debye-Scherrer formula, while lattice constants were calculated using the (220) peak based on a combination of Bragg’s law and the relationship between lattice and crystal-lattice spacing as follows:

\[
L = \frac{0.9 \lambda_{K\alpha}}{B_2 \theta \cos \theta_{max}}
\]

where \( L \) is the mean crystallite size, \( \lambda_{K\alpha} \) is the X-ray wavelength (1.5406 Å), B is the full width of the peak (rad) at half-maximum (FWHM), and \( \theta_{max} \) is the Bragg angle (rad) of (220) peak position.
5.3.3 Half-cell tests

A traditional three-electrode water-jacket-integrated glass cell (AFCELL3, Pine Instrument) with a glassy carbon working electrode (AFE3T050GC, Pine Instrument), a Hg/HgO reference electrode (MMO, CHI152, CH Instruments), and a platinum wire counter electrode (AFCTR1, Pine Instrument), were used for cyclic voltammetry (CV). All tests were prepared and performed at ambient temperatures and all potentials were specified to MMO (1.0 M KOH, 0.098 V vs. SHE). The prepared catalysts were dispersed by ultrasonication in 1-propanol to form a uniform ink (0.5 mg mL$^{-1}$). The working electrode was prepared by polishing a glassy carbon electrode (GCE) with alumina micropolish solution and grinding paper to produce a mirror-polished surface. 10 µL of ink were deposited drop wise onto the surface of GCE and the electrolytes were composed of 1.0 M KOH + 0.1 M glucose, levoglucosan, or sucrose in deionized water. Cyclic voltammetry was performed at a constant sweep rate of 50 mV s$^{-1}$ with nitrogen gas purging.

5.3.4 Single cell tests

Fuel cell tests were performed on a Scribner Fuel Cell System 850e (Scribner Associates, USA), [29, 32, 33]; the fuel cell fixture with an active area of 5 cm$^2$ was purchased from Fuel Cell Technologies, Inc. The anode catalyst layers were prepared by spraying catalyst ink onto untreated carbon cloth with catalyst loading of 0.5 mg$_{metal}$ cm$^{-2}$ with a binder ratio of 9:1 PTFE. The cathode catalyst substrate was constructed by spraying 3 mg cm$^{-2}$ non-noble metal loading commercial catalyst (4020 Acta) with an ionomer ratio of 7:3 (AS-4, Tokuyama Corp.) on an anion exchange membrane (A901, Tokuyama Corp). Liquid fuel was pumped into the anode compartment at a flow rate of 4.0 mL min$^{-1}$ while high purity O$_2$ was fed into the cathode compartment at a flow rate of 200 mL min$^{-1}$ under a
backpressure of 0 psig. The liquid fuel, the O\textsubscript{2}, and the reactor were maintained at constant temperature.

5.3.5 Chemical analysis
5.3.5.1 High performance liquid chromatography

Non-volatile sugars were characterized using an HPLC equipped with a refractive index (RI). A Bio-Rad Aminex HPX-87P with a guard column was used in the set-up. The column temperature was 75°C with a deionized-water flow rate of 0.6 mL/min 18.2 Ω. The RI detector required calibration for non-volatile sugars diluted with deionized water into five concentrations (0-10 mg/mL). Approximately 1.0 g of bio-oil sample was dissolved in 5 mL of deionized water and thoroughly mixed with a vortex mixer for 20 min. The well-mixed solution was then filtered through a Whatman® 0.45 µm glass microfiber filter and a 25 µL sample was injected into the HPLC; the total run for time each sample was 70 min. The bio-oil chemical analysis used methods similar to those developed by Pollard [19] and Choi [34].

5.3.5.2 Ion chromatography

Thermally labile organic acids were characterized by Ion Chromatography (IC) using a Dionex ICS3000 equipped with a conductivity detector and an Anion Micromembrane Suppressor AMMS-ICE 300. The suppressor regenerant was 5 mM tetrabutylammonia hydroxide at a flow rate of 4-5 mL/min. The mobile phase utilized 1.0 mM heptafluorobutyric acid in an IonPac® ICE-AS1 analytical column at a flow rate of 0.120 mL/min at 19°C. The diluted mixture was filtered through a Whatman ® 0.45 µm glass
microfiber filter and 25 µL were injected into the IC; the total run time for each sample lasted 70 min.

5.3.5.3 Gas chromatography

Volatile compounds in the bio-oil were characterized by Gas Chromatography using a Mass Spectrometer (GC-MS) for identification. The column used for this setup was a Zebron ZB-1701 coated with 14% cyanopropylphenyl and 86% dimethylpolysiloxane with dimensions of (60 m x 0.25 mm ID x 0.25 µm film thickness). The oven was programmed to hold a steady temperature at 35°C for 3 min, ramp up at 5°C/min to 300°C, and then hold steady for 4 min. The injector of GC was maintained at 300°C and engaged a split ratio of 30:1. The flow rate of helium carrier gas was 1 mL/min. The mass spectrometer was configured for electron impact ionization, with a source/interface temperature of 280°C. Full-scan mass spectra were acquired from 35 to 650 m/z at a scan rate of 0.5 s per scan, and compounds were identified using a NIST mass spectra library search consistent with the literature.

5.3.5.4 Proton nuclear magnetic resonance

$^1$H NMR spectra were collected with a Bruker 600 MHz NMR (AVIII600); the temperature was regulated to 25°C during the acquisition and $^1$H NMR spectra were acquired at room temperature. The bio-oil sample preparation was prepared by drying 50-100 mg of bio-oil for 48 hours. The dried sample was reconstituted with 1 mL Deuterium oxide and the resultant solution was filtered with 0.2 µm filter paper. The data was analyzed using MestReNova version 8.1 software.
5.4 Results and discussion
5.4.1 Physical characterization of catalysts

Fig. 5.1 (a-d) shows the TEM images and the corresponding metal particle size histograms of Pt, Pd, Au, and Ag nanoparticles supported on CNTs. It is observed that well-dispersed metal particles uniformly deposited on the CNT support, and the average particle sizes, determined by randomly measuring 100 particles, were 1.4, 2.0, 3.8, and 12.9 nm for Pt/CNT, Pd/CNT, Au/CNT, and Ag/CNT, respectively. The particle size distributions are fairly narrow: 0.5-4.0 nm for Pt, 1.0-4.0 nm for Pd, 2.0-6.5 nm for Au, except for Ag: 6-22 nm. Roughly big particle agglomerations were found on Ag/CNT sample. Fig. 5.1 (e) depicts the XRD patterns of Pt/CNT, Pd/CNT, Au/CNT, and Ag/CNT. The XRD patterns show that the metal particles have a face-centered cubic (FCC) structure, with diffraction peaks of (111), (200), (220), and (311) facets, respectively. The mean crystal size values, calculated from using the Debye-Scherrer formula [35-37], were 1.3 nm, 2.0 nm, 4.1 nm, and 13.9 nm for Pt/CNT, Pd/CNT, Au/CNT, and Ag/CNT, respectively, in good agreement with the TEM results. The aqueous-phase reduction method used in this study can prepare very small Pt and Pd nanoparticles under these conditions, however, lead to relatively large Au and Ag nanoparticles, and their optimal synthesis conditions need to be further optimized. Ag precursor is not fully reduced by sodium borohydride (reducing agent) due to Ag (+0.80 V) having a lower standard redox potential than Pt (+1.20 V), Pd (+0.99 V), and Au (+1.50 V). There is also a lack of surfactant (capping agent) in an aqueous-phase reduction method. The surface energy is one of the most important factors affecting the average particle size of the nanoparticles, especially when no strong capping agent is added during preparation. As can be seen in Fig. S5.1 and Fig. S5.2 of Supplementary Information (SI), the surface free energy is a logarithmic function of the number of atoms presented in
the particle. When the surface free energy of a Pt, Pd, Au, and Ag particle is relatively stable, the total energy required follows the sequence Pt>Pd>Au>Ag. The more energy required, the harder for the atoms to agglomerate. Therefore, the average particle size sequence is Ag>Au>Pd>Pt.

Fig. 5.1 TEM and histograms of (a) Pt/CNT, (b) Pd/CNT, (c) Au/CNT, (d) Ag/CNT, and (e) XRD patterns of Pt/CNT, Pd/CNT, Au/CNT, and Ag/CNT.
5.4.2 Compositional analysis of bio-oil fraction

Due to bio-oil complexity, bio-oil fractions obtained from fast pyrolysis were analyzed using a broad range of analytical techniques. Significant process descriptions of various analytical techniques dealing with analysis of bio-oil have been reported in the literature [17, 38, 39]. In this study, to understand and design an AEMFC with fast pyrolysis bio-oil, it was necessary to obtain knowledge of major and active components of bio-oil. HPLC was used to detect non/semi volatile sugars with high molecular weight compounds, such as levoglucosan, celllobiosan, and xylose. Levoglucosan was found to be the major identified sugar compound, representing 11.1 wt% of the bio-oil. IC rather than gas chromatography was used to detect carboxylic acids because of thermal instability of organic acids. The bio-oil consisted of approximately 3.3 wt% of organic acids, including acetic, propionic, glycolic and formic acids. Table 5.1 lists quantified distributions of sugars and organic acids using HPLC and IC. The complete quantification was done using IC and HPLC for detection of carboxylic acids and heavy sugars such as mono/disaccharides.

Table 5.1 Distributions of fast pyrolysis bio-oil by HPLC and IC.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HPLC detectables</strong></td>
<td></td>
</tr>
<tr>
<td>Cellobiose</td>
<td>0.35</td>
</tr>
<tr>
<td>Celllobiosan</td>
<td>3.35</td>
</tr>
<tr>
<td>Xylose</td>
<td>2.30</td>
</tr>
<tr>
<td>Galactose</td>
<td>0.50</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>11.10</td>
</tr>
<tr>
<td><strong>IC detectables</strong></td>
<td></td>
</tr>
<tr>
<td>Glycolate</td>
<td>1.35</td>
</tr>
<tr>
<td>Formate</td>
<td>0.75</td>
</tr>
<tr>
<td>Acetate</td>
<td>0.56</td>
</tr>
<tr>
<td>Propionate</td>
<td>0.67</td>
</tr>
</tbody>
</table>
GC was used to characterize volatile compounds of bio-oil. The resulting analysis for the bio-oil, as shown in Table S5.1 of SI, demonstrated that the majority of identified compounds from GC are in the categories of furans, ketones, hydroxylaldehydes, alcohols, carboxylic acids, and phenolics. The compound identification from GC was relatively consistent with previous work by Brown et al. [19, 20, 34]. Volatile compounds present in the bio-oil detected by GC were in very small quantities, less than 0.01 wt%, so in this analysis further detailed quantitative identification of compounds in the bio-oil was not intended to be exhaustive. Further investigations were carried out on analysis of bio-oil by proton nuclear magnetic resonance ($^1$H NMR) spectroscopy to confirm the identification of levoglucosan present in the bio-oil. Fig. S5.3 of SI shows $^1$H NMR spectra to confirm the identification of levoglucosan as the major component of crude bio-oil.

5.4.3 AEMFC with direct fast pyrolysis bio-oil
5.4.3.1 Effect of catalyst on AEMFC performance

Our primary goal is to explore the feasibility of low temperature AEMFC with noble metal catalysts for direct electricity generation from crude fast pyrolysis bio-oil. From both real-world engineering and application point-of-view, single fuel cell is an ultimate platform for catalyst performance test. Fig. 5.2a displays the cell polarization and power density curves of direct bio-oil AEMFC using the Pd/CNT, Ag/CNT, Au/CNT, and Pt/CNT anode catalysts. The open circuit voltage (OCV) of the direct bio-oil AEMFC with Pd/CNT was 0.84 V, which is 0.04 V higher than that with Ag/CNT, 0.05 V higher than that with Pt/CNT, and 0.09 V higher than that with Au/CNT. The peak power density (PPD) of the direct bio-oil AEMFC with Pd/CNT was 42.7 mW cm$^{-2}$, which is 4.5% higher than that with Pt/CNT, 8.7% higher than that with Ag/CNT, and 10.2% higher than that with Au/CNT. It is worth
to mention that bio-oil, a complex mixture of more than 400 compounds, can be directly used as renewable fuel in AEMFCs without the need of catalytic conversion of bio-oil into fuel. Although our results indicate that there is no significant difference among the four noble catalysts (see Fig. 2a), Pd/CNT anode catalyst shows slightly higher fuel cell performance than the others. This is consistent with well-known understanding that Pd electrocatalysts are exclusively active for alcohol oxidation reaction and hydrogen oxidation in alkaline media [40, 41]. We hypothesize the current generated on Pd/CNT is mainly attributed to the oxidation of levoglucosan and partially to oxidizing other compounds present in the bio-oil, especially sugars and alcohols. Ag is well-known for electrochemically catalyzing the carbonyl group (aldehyde and ketone) oxidation reaction more efficiently than Pt/CNT, Pd/CNT, and Au/CNT [42]. Therefore, the current generated on Ag/CNT may be attributed to the Ag nanoparticle’s electrocatalytic activity of aldehyde groups present in the bio-oil.

We studied electrocatalytic oxidation of the model biomass molecule hydroxymethylfurfural (HMF), and found that Au greatly favors aldehyde oxidation over alcohol oxidation, but high electrode potentials are required for further oxidation of alcohol groups with Au [43], these preferences may also exist in complicated bio-oil electro-oxidation processes. It is well known that Pt is active to organic molecules electro-oxidation and can even facilitate spontaneous breakage of C-C bonds [44, 45]. The direct fast pyrolysis bio-oil fuel cell with all the four catalysts Pd/CNT, Ag/CNT, Au/CNT, and Pt/CNT shows quite high open circuit voltage (OCV), conforming the overpotential to be sufficiently low to deliver current. This is because the catalysts can catalytically oxidize few of the compounds with their favored functional groups in the bio-oil. More than one functional group and highly active compounds in bio-oil impulsively play a significant role towards achieving AEMFC
performance. We have demonstrated Au/C with different particle sizes (3.0 nm vs 4.7 nm); no obvious difference was observed between two DGFC with Au/C with particle sizes of 3.0 nm and Au/C with 4.7 nm [46]. For a direct pyrolysis bio-oil fuel cell, we similarly do not observe any apparent particle size effect on fuel cell performance. Future research will be to examine the bio-oil composition change due to electro-oxidation, so as to identify the main reactive components over the four catalysts, thus better bimetallic electrocatalysts may be rationally designed to achieve higher fuel cell power density.

5.4.3.2 Effect of temperature on AEMFC performance

Fig. 5.2b shows the cell polarization and power density curves of direct bio-oil AEMFC with Pd/CNT operated at various temperatures; the cell performance increased as the temperature increased over the whole current density range. In particular, the limiting current density increased from 120 to 290 mA cm\(^{-2}\) when the temperature was increased from 25°C to 80°C. This increase in temperature enhances the electrochemical kinetics of both the bio-oil oxidation reactions at the anode and the oxygen reduction reaction (ORR) at the cathode. The OCVs of direct bio-oil AEMFC operating at 25, 40, 60 and 80°C were 0.66, 0.72, 0.79, and 0.81 V, while the PPDs were 12.4, 17.1, 25.2, and 34.0 mW cm\(^{-2}\), respectively. In addition, the electrolyte conductivity increases with increasing temperature, reducing the ohmic loss, as shown by the cell resistance in Fig. S4a of SI. It has been demonstrated that the cell resistance is decreased as the temperature is increased and the resulting cell performance is improved. Furthermore, both bio-oil and oxygen transport diffusivities increase with an increased temperature, resulting in low mass transport polarization, so the cell performance increases as the temperature is increased; this can be
attributed to faster electrochemical kinetics, increased conductivity of hydroxyl ions, and enhanced mass transfer.

Fig. 5.2 a-d polarization and power density curves of bio-oil AEMFC (a) comparison of different noble metal catalysts, 80°C; b) effect of temperature on Pd/CNT; c) effect of KOH concentration on Pd/CNT, 60°C; d) effect of bio-oil concentration on Pd/CNT, 60°C.

5.4.3.3 Effect of KOH concentration on AEMFC performance

As shown in Fig. 5.2c, the fuel cell performance in terms of cell voltage increases from 1.0 to 6.0 M with increasing KOH concentration, then decreases as the KOH
concentration further increases beyond 6.0 M. The peak power densities plotted against KOH concentration exhibits a volcano-type behavior. In general, an increase in electrolyte alkalinity leads to higher local OH\textsuperscript{-} concentration at the anode catalyst layer and higher OH coverage on the catalyst surface, facilitating electrochemical kinetics [47-50]. The electrical conductivity of the KOH water solution will first increase and then decrease as KOH increases from 0 M to 12.0 M; it reaches its maximum value at 7.0-8.0 M [51]. Thereupon, the single cell IR decreases as KOH concentration changes from 0 M to 8.0 M and then increases when KOH concentration further increases beyond 8.0 M, as shown in Fig. S4b of SI. If the KOH concentration was further increased beyond 8.0 M, large KOH concentration would have led to an excessive surface coverage with hydroxyl ions, thereby decreasing the number of active catalytic sites available for bio-oil absorption and causing the IR to increase while the cell voltage and associated performance declined. The maximum KOH concentration is limited due to its solubility in bio-oil solution. It is known that in AEMFC the internal resistance is affected by both anode and cathode membrane due to the conductive resistance of hydroxyl anions from cathode to anode side. We previously reported this phenomenon [29], stating that a surplus of hydroxyl anions will prevent fuel from being sufficiently absorbed onto the active sites of an anode catalyst layer. High internal resistance is thus observed at beyond 8.0 M KOH due to the mass transfer issue becoming dominant. In summary, it can be concluded that single-cell performance increases with an increased KOH concentration until reaches a maximum limitation by the excessive hydroxyl ions coverage and decrease in the number of active catalytic sites.
5.4.3.4 Effect of bio-oil concentration on AEMFC performance

Fig. 5.2d illustrates that fuel performance and cell voltage increase with higher concentration of bio-oil at low current density as the local bio-oil concentration increases from 5.0 wt% to 30.0 wt% (equivalent levoglucosan concentration: 0.3 M). A further increase in the bio-oil concentration from 30.0 wt% to 60.0 wt% causes the cell voltage to decrease gradually in the low current density region. In addition, higher bio-oil concentration causes the more active sites of the anode catalyst to be covered by the bio-oil, blocking the adsorption of hydroxide on the active sites and leading to a decrease in performance. Essentially, the kinetics of the oxidation reaction depends on the surface concentration of both bio-oil and hydroxide ions. At higher current densities, the cell voltage dropped more rapidly for 5.0 wt% concentration than with 20 to 40 wt% concentration because a 5.0 wt% supplies a mass transfer rate insufficient to produce high current densities; the bio-oil concentration in the anode catalyst layer is simply inadequate. Cell performance also declines when the bio-oil level is higher than 30 wt%; this concentration of bio-oil alleviates diffusion limitations due to the higher driving force required for mass transport. However, when the bio-oil concentration is increased, the electrolyte viscosity increases, decreasing the OH⁻ mobility and conductivity of the electrolyte. An increase in cell resistance with increasing bio-oil concentration is shown in Fig. S4c of SI. The higher bio-oil concentration (40.0-60.0 wt%) creates a barrier for OH⁻ transfer by covering active sites in the anode catalyst layer, leading to an extreme increase in cell resistance, from 198.3 mΩ to 316.2 mΩ. This extreme cell resistance causes a reduction in the cell voltage and the cell performance is thus reduced. In summary, OCV and cell performance increases with an increase of bio-oil concentration of up to 30 % because the local bio-oil concentration in the catalyst layer
is too low. However, when the bio-oil fuel solution is too high at the anode catalyst layer, the coverage of hydroxide ions on catalytic sites is reduced, producing dramatic decreases in cell performance and cell voltage.

5.4.4 Electrooxidation of levoglucosan over various catalysts in half-cell

Since levoglucosan has been identified as the major component present in bio-oil, the activity of electrocatalytic oxidation of levoglucosan on Pd/CNT, Ag/CNT, Au/CNT, and Pt/CNT was investigated in a three-electrode half-cell system. The reason for this investigation was to further understand the catalyst mechanism of an identified levoglucosan in bio-oil. Fig. 5.3 shows that the Pd/CNT catalyst exhibited higher current density than Ag/CNT, Au/CNT, and Pt/CNT at low potential (below 0.0 V) despite its small hydrogen adsorption-desorption properties. Furthermore, Pd/CNT exhibited a more negative onset potential (-0.4 V) compared to those of Pt/CNT (-0.3 V), Au/CNT (-0.05 V), and Ag/CNT (0.1 V). The sequence of onset potential in the forward scan was Pd/CNT<Pt/CNT<Au/CNT<Ag/CNT; this is consistent with AEMFC performance results. However, a low anode overpotential is preferred in the fuel cell operation, and the low potential region (<0.7 V vs. RHE vs. -0.2 V vs. Hg/HgO) is more important than the resulting high potential region of CV. Au/CNT demonstrates an extremely high peak current density at high potential, indicating that the Au catalyst can maintain its activity over a wide applied potential range. Au/CNT, Ag/CNT and Pt/CNT catalysts displaced very little to no activity toward levoglucosan electro-oxidation at lower potentials.
Fig. 5.3 Cyclic voltammograms of levoglucosan oxidation reaction on Pd/CNT, Ag/CNT, Au/CNT, and Pt/CNT catalysts in 1.0 M KOH + 0.1 M levoglucosan, 50 mV s\(^{-1}\), 25°C.

5.4.5 Electrooxidation of high purity sugars over Pd/CNT in half-cell and AEMFC

To compare the performance of electrocatalytic oxidation of sugars, the activity of electrocatalytic oxidation of high purity sugars such as glucose, levoglucosan, and sucrose on Pd/CNT was investigated in both half-cell and single fuel cell configurations. Fig. 5.4 shows that the current density for glucose was slightly higher than that for levoglucosan. Generated current density from glucose and levoglucosan oxidation was much greater than that from sucrose oxidation. Glucose and levoglucosan are both C\(_6\) molecules and can be adsorbed on the thin catalyst film faster, exposing more active sites to the fuel than the C\(_{12}\) molecules of sucrose. Smaller species generally have better mass transfer and can be adsorbed faster on the catalyst thin film compared to bigger species with poor mass transfer [52, 53]. Sucrose is adsorbed more slowly on the active sites of the catalyst, further diminishing occurrence of fully oxidation to occur. Furthermore, electrooxidation of glucose
exhibited more negative onset potential (-0.6 V) compared to levoglucosan (-0.4 V), and sucrose (-0.3 V); this may be attributed to the relatively more active aldehyde group in glucose.

Fig. 5.5 shows the cell polarization and power density curves of direct high-purity sugar-fed AEMFCs with Pd/CNT as an anode catalyst. The OCV of direct high-purity sugar-fed AEMFC operating with glucose, levoglucosan, and sucrose are 0.96, 0.83, and 0.79 V, while the PPD values are 145.5, 73.6, and 49.1 mW cm$^2$, respectively. As demonstrated, the output power dramatically drops when AEMFC is fueled with the higher carbon-chain sugar such as sucrose. These single cell results on direct high-purity sugar-derived AEMFCs are consistent with our previous findings for half-cells. Glucose and levoglucosan are both adsorbed on the anode catalyst layer faster than sucrose, revealing that glucose and levoglucosan has a higher permeability that facilitates the species transport, lowering transport resistance, resulting in the enhanced mass transport, thus higher peak power density was obtained.
5.4 The relationship between fast pyrolysis bio-oil fuel cell and sugar fuel cell

The peak power density of bio-oil fuel cell is about ~ 1.2 to 3 times lower than that of a high-purity sugar fuel cell with the same Pd loading, considering that the equivalent sugar content in bio-oil is only about 0.3 M sugar. Many unknown and highly active compounds containing aldehyde, furans, phenolics, and ketone groups in bio-oil may play significantly different roles in performance of AEMFCs. The generated current in direct bio-oil fuel cells using all four noble metals is attributed to many spontaneous and simultaneous oxidation processes. It is interesting to find that the inert impurities of bio-oil do not poison the noble metal catalyst and therefore do not deactivate the catalyst. The limiting current densities on the direct bio-oil AEMFC also do not significantly drop with enormous variations (Fig. 5.2a), indicating that complex mixtures of bio-oil lead similarly do not have poor mass transfer phenomenon with all tested catalysts. Our recent work further shows that
using N and S-doped mesoporous carbon as metal-free cathode catalysts [54] and a robust PTFE porous separator [55] as an electrolyte membrane can significantly reduce the cost of the fuel cell, while maintaining similar fuel cell performance. Overall, we have demonstrated a direct bio-oil fuel cell can directly generate electrical energy from complex bio-oil without any purification process. The electrical power density is nearly 2 orders of magnitude greater than reported enzymatic biofuel cell with high-purity derived sugars [56, 57]. Our results may provide a new route to directly generating high power density electricity from bio-oil, and further offer an electrochemical processing approach for bio-oil upgrading to valuable chemicals from the bio-oil fuel cell anode downstream.

Fig. 5.5 The polarization and power density curves of direct high-purity sugars derived AEMFC with Pd/CNT anode catalyst; Fe-based Acta 4020 cathode catalyst; anode fuel: 6.0 M KOH + 0.5 M glucose, levoglucosan, and sucrose; 80°C.
5.4.7 Research and development efforts for the future direct pyrolysis bio-oil fuel cell

This new technology proves that fast pyrolysis bio-oil as alternative fuel for fuel cells and crude feedstocks expand fuel sources for fuel cell applications. Direct fast pyrolysis bio-oil fuel cells can be economically beneficial if “bio-oil upgrading” and “electricity generation” can be simultaneously achieved. Efficient and direct production of electricity from raw biomass feedstock can be considered as a supplement to current thermochemical, chemical, and biological methodologies for transforming biomass to energy and chemicals, thus reducing subsequent purification costs. Techno-economic analysis (TEA) can provide economic indicators for future bio-oil fuel-cell materials and technology development. There are, however, major areas that should be improved if bio-oil is to become a reliable energy source in fuel cell technologies. These research include: (i) develop advanced anode catalysts that can improve the electrocatalytic oxidation and stabilization of bio-oil, while alleviating catalyst poisoning and degradation, (ii) explore low cost efficient cathode catalyst that is active to oxygen reduction reaction but inactive towards bio-oil, (iii) study reliable, inexpensive anion exchange membranes with minimized reactant crossover, and (iv) understand the reaction steps and pathways so as to design more efficient electrocatalytic processes. This novel electrochemical system concept will help renovate how we produce, transport, or use energy, and facilitate combining renewable electricity and carbon sources to achieve green electrocatalytic manufacturing and electrical energy generation.

5.5 Conclusions

In this work, we have demonstrated that bio-oil can be directly used as a fuel for AEMFCs at low temperatures. A direct bio-oil AEMFC using CNT supported noble metal nanoparticles (Pt/CNT, Pd/CNT, Au/CNT, or Ag/CNT) as an anode catalyst achieved a
remarkably high peak power density of 42.7 mW cm\(^{-2}\) at 80°C and ambient pressure. In addition, the effects of variation in operating conditions, including bio-oil concentration, temperature, and KOH concentration, were investigated to further enhance performance of the fuel cell. The highest performance was achieved with 6.0 M KOH and 30 wt% bio-oil at 80°C on Pd/CNT. The experimental results showed that cell performance improves with optimized operating parameters due to the improved kinetics of ORR, and an increase in bio-oil diffusivity and hydroxyl ion conductivity. The compositional analysis of bio-oil was performed using HPLC, GC, and IC analytical techniques. Levoglucosan was found to be the major identified sugar compound of the bio-oil, with 11.1 wt%. The electrocatalytic activities of four noble previous catalysts (Pd/CNT, Ag/CNT, Au/CNT, and Pt/CNT) on highly-purified sugar (levoglucosan) identified by cyclic voltammetry showed that Pd/CNT had the highest activity in the low potential region with lowest onset potential. The relationship between pyrolysis bio-oil and a pure sugar fuel cell shows that bio-oil fuel cell is about ~ 1.2 to 3 times lower than the high purity sugar fed fuel cell. The direct bio-oil AEMFC, however, has potential due to its capability of using unrefined biomass-derived feedstock for fuel.

5.6 Acknowledgements

We acknowledge financial support from the US National Science Foundation (CBET-1159448, 1501124) and the Iowa State University startup fund. The authors would like to thank Ryan Smith for supplying bio-oil and John Matthiesen, and Dr. Robert L. Johnson of Iowa State University for assistance in understanding NMR data analysis.
5.7 References


[55] Benipal N, Qi J, Gentile JC, Li W. Direct Glycerol Fuel Cell with Polytetrafluoroethylene (PTFE) Thin Film Separator Manuscript in progress


Table S 5.1 Identified compounds of fast pyrolysis bio-oil by GC.

<table>
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<th>Compounds</th>
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<tr>
<td><strong>Furans</strong></td>
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<tr>
<td>2-Furan methanol</td>
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<tr>
<td>2-(5H)-Furanone</td>
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<td>4-Methyl-5H-furan-2-one</td>
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<tr>
<td>5-Hydroxymethylfurfural</td>
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<tr>
<td><strong>Ketones</strong></td>
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<tr>
<td>1-Hydroxyl-2-Propanone</td>
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<td>1-Hyrdoxy-2-Butanone</td>
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<tr>
<td>2H-pyran-2-one</td>
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<td><strong>Aldehydes</strong></td>
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<td>Acetaldehyde</td>
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<td>Vanillin</td>
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<td>Formaldehyde</td>
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<td>Glycolaldehyde</td>
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<td><strong>Alcohols</strong></td>
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<tr>
<td>1,3 Propanediol</td>
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<td>Acetol</td>
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<tr>
<td>Methanol</td>
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<td><strong>Phenols</strong></td>
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<td>Vanillin</td>
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<td>2-Methoxyphenol</td>
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<td>2-Methylphenol</td>
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<td>3,4-Dimethylphenol</td>
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<td>Eugenol</td>
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<td><strong>Benzenediols</strong></td>
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<td>Hydroquinone</td>
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<td>t-Butylhydroquinone</td>
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Fig.S.5.1 Size dependent surface free energy of Cu, Ag, Au, and Pt nanoparticles [1].

Fig.S.5.2 Size dependent surface free energy of W, Ta, Mo and Pd nanoparticles [1].
Fig.S.5.3 NMR Spectra of levoglucosan in bio-oil.
Fig. S.5.4 Open-circuit voltages and cell resistance curves of direct bio-oil fuel cell. a) effect of temperature b) effect of KOH concentration, c) effect of bio-oil concentration.
5.8.1 References

CHAPTER 6 DIRECT GLYCEROL FUEL CELL WITH POLYTETRAFLUOROETHYLENE (PTFE) THIN FILM SEPARATOR

Graphical abstract for “Direct glycerol fuel cell Polytetrafluoroethylene (PTFE) thin film separator” published as a TOC in applied catalysis B: environmental journal.

*The material contained in this chapter is published in Renewable Energy Journal, Jan 2017, currently waiting on reviewer’s comments: “Direct Glycerol Fuel Cell with Polytetrafluoroethylene (PTFE) Thin Film Separator” by Neeva Benipal, Ji Qi, Jacob C. Gentile, Wenzhen Li
6.1 Abstract

Anion-exchange membrane-based direct glycerol fuel cells (AEM-DGFCs) can yield high power density, however challenges exist in developing chemically stable AEMs. Here, we demonstrate a porous polytetrafluoroethylene (PTFE) thin film, a well-known chemical, electro-chemical, and thermal robust material that can serve as a separator between anode and cathode, thus achieving high DGFC’s performance. A simple aqueous-phase reduction method was used to prepare carbon nanotube supported PdAg nanoparticles (PdAg/CNT) with an average particle size of 2.9 nm. A DGFC using a PTFE thin film without any further modification with PdAg/CNT anode catalyst exhibits a peak power density of 214.7 mW cm\(^{-2}\) at 80°C, about 22.6% lower than a DGFC using a state-of-the-art AEM. We report a 5.8% decrease and 11.1% decrease in cell voltage for a PTFE thin film and AEM; similarly, the cell voltage degradation rate decreases from 1.2 to 0.8 mV h\(^{-1}\) for PTFE thin film, while for AEM, it decreases from 9.6 to 3.0 mV h\(^{-1}\) over an 80 h durability test period. Transmission electron microscopy results indicate that the average particle size of PdAg/CNT increases from 2.9 to 3.7 nm after 80 h discharge; this suggests that PdAg particle growth may be the main reason for the performance drop.
6.2 Introduction

Fuel cells are environmentally-friendly devices for energy conversion and power generation, and are often regarded as one of the promising advanced energy technologies of the future. Recently, direct alcohol fuel cells (DAFCs) have attracted considerable interest in application to alternative power sources because of their high volumetric energy density, easy transport, and convenient handling [1-7]. In DAFCs, the chemical energy stored in the alcohol fuel is directly converted into electrical energy without the limitation of Carnot’s theorem [8, 9]. Among all the alcohols, methanol and ethanol [10-14] have been most widely investigated in fuel cell applications due to their well-known reaction mechanisms and relatively high theoretical energy densities (4.6 and 6.1 kWh L\(^{-1}\)). However, the toxicity of methanol and high volatility of ethanol remain critical issues under practical operation conditions, so glycerol has been considered as a promising alternative fuel for DAFCs because of its relatively low price, convenient storage, non-volatility, non-flammability, and highly-functionalized molecule with a theoretical energy density of 6.4 KWh L\(^{-1}\).

Proton exchange membrane (PEM) based DAFCs employ high loading (e.g. > 2.0 mg cm\(^{-2}\)), at both anode and cathode of precious metals such as Pt or PtRu. By comparison, anion-exchange membrane (AEM) based DAFCs have the great advantage that both the kinetics of alcohol oxidation and oxygen reduction at the anode and cathode can be greatly improved; in particular, non-noble metals, such as Fe, Co, and Ni macrocycles, can serve as cathode catalysts, significantly reducing the overall DAFC system cost [15-19]. Various studies have widely used platinum-based catalyst in low-temperature PEM-DAFCs [12, 20]. Although Pt’s catalytic activity with respect to alcohols such as methanol [10], ethanol [21],
glycerol [22], and ethylene glycol [23] can be very high in DAFCs, the high cost due to scarcity of Pt is problematic. Extensive efforts are therefore being carried out to design new catalysts for DAFCs and palladium is emerging as an attractive replacement for platinum in AEM-DAFCs because it is more abundant in nature and less expensive than Pt. Unlike Pt or Pt-based electrocatalysts, Pd can be highly active for oxidation of a large variety of substrates in an alkaline environment. To prepare Pd-based electrocatalysts, intensively studies have been conducted over the past few years with the aim of increasing catalyst activity, controlling the morphology of Pd, enlarging the surface area, and improving catalyst stability [2, 24-27]. In particular, the addition of Ag to Pd/CNT significantly promotes catalytic activity for the electrooxidation of glycerol and also reduces the cost of the anode catalyst. We have recently demonstrated that a PdAg catalyst [28] can perform very well, especially in terms of current density, and has capability for cleaving C-C bonds for long-chain alcohols oxidation.

Past research studies have mainly focused on the development of designs and materials used in a fuel cell system [29-31]. A current major challenge in commercialization of fuel cell technology lies in the development of new durable membranes that will allow fuel cell operation at high temperatures without extensive humidification requirements. Traditional low-temperature fuel cells rely on ion-exchange membranes that, as the “heart of the DAFCs”, have an essential function of separating reactions at both anode and cathode, allowing only H⁺ or OH⁻ (or other anions, such as CO₃²⁻) to freely move across PEM or AEM, respectively. The most common AEMs require properties such as high OH⁻ conductivity, good chemical/thermal stability. Durability and operating stability of AEMs are becoming issues because of faster degradation at elevated temperatures and harsh
conditions of alkaline electrolytes [32-35]. Choban, et al., [36] reported laminar-flow-based membraneless fuel cells. Cohen, et al., [37] also demonstrated membraneless microchannel fuel cells that utilized laminar flow in microchannels to segregate fuel and oxidant to overcome design limitations caused by the use of PEM. Hou, et al., [33] studied a KOH-doped polybenzimidazole membrane as a polymer electrolyte membrane in direct ethanol fuel cells. It enhanced the ionic conductivity of the membrane and also decreased ethanol permeability to much less than that of Nafion membranes. Mota, et al., [38] reported use of an unconventional barrier, a polycarbonate filter paper, to separate fuel and oxidant streams in a microfluidic fuel cell. This barrier allowed diffusive transport through its pores while preventing crossover of the fuel and oxidant streams. Yang, et al., has demonstrated a peak power density of 663 mW cm$^{-2}$ using a polymer fiber membrane (PFM) as a separator replacing the polymer electrolyte membrane in direct borohydride fuel cells. The fiber materials in the PEM are made of polypropylene, polyamide, or polyvinyl alcohol, and act as a very thin liquid electrolyte layer that allow the anions and cations, including BH$_4^-$, OH$^-$, and Na$^+/K^+$, to flow across freely [39]. Cost analysis of PEM fuel cells using hydrogen or methanol as fuels has shown that the price of membranes usually contributes 8 to 10 % of the manufacturing cost of a fuel cell stack [40], but challenges still exist in the development of chemically stable ion-exchange membranes, representing a major technical obstacle hindering the commercialization of AEM-DAFCs.

It has been established that the state-of-the-art AEMs and PEMs are not indispensable for fuel cell operation, and several alternative membranes have been used to replace the state-of-the-art membranes [41-43]. Nafion/PTFE composite membranes produced by various synthesizing methods have been developed for fuel cell applications [44-46]. These
composite membranes were synthesized by impregnating porous PTFE membranes with a self-made Nafion solution. The fluorocarbon bond in the PTFE is strong, with a very high molecular weight and a high melting point (327°C). PTFE thin films are chemically and biologically inert, stable up to 260°C, and can withstand most concentrated acids and bases. PTFE thin films permit diffusive transport through their pores while preventing mixing of fuel and oxidant streams. Access to PTFE thin films promises important benefits with respect to complexity, cost, and performance of the fuel cell systems.

In this study, we investigated DGFC using PTFE thin films with different pore sizes as potential separators in high alkaline electrolyte to provide electrical insulation between cathode and anode. Subsequently, a comparison of DGFC with PTFE thin film and anion-exchange membrane (A901) has been performed. Furthermore, a durability test was performed to evaluate the cell voltage degradation rate of both PTFE thin film and A901 anion-exchange membrane-based DGFCs. The anode degradation on PdAg/CNT was evaluated using a transmission electron microscope.

6.3 Experimental
6.3.1 Chemicals

Palladium (II) nitrate dihydrate (40%), silver nitrate (99%), 1-propanol (99.5%), potassium hydroxide (85%), potassium sulfate (99%), polytetrafluoroethylene (PTFE) ionomer solution (60%), sodium borohydride (99%), sodium citrate dihydrate (99%), and glycerol (99.5%) were purchased from Sigma-Aldrich. Carboxyl-group functionalized multi-wall carbon nanotubes (8-15 nm outer diameter, 0.5-2 μm length) were bought from Cheaptubes, Inc. The cathode catalyst 4020 was obtained from Acta, Inc. PTFE thin films
with pore sizes 0.22, 0.45, and 1.0 µm were obtained from Membrane Solutions. All chemicals were used as received without further purification.

6.3.2 Synthesis of catalysts and physical characterizations

PdAg/CNT (20 wt%) was prepared via a self-developed aqueous-phase reduction method [6, 47]. Briefly, Palladium (II) nitrate dihydrate (56 mg) and silver nitrate (35.7 mg) were dissolved together in deionized water (1500 mL). Sodium citrate dihydrate (200 mg) and sodium borohydride (40 mg) were each separately dissolved in deionized water (50 mL) and carboxyl-group functionalized multiwall carbon nanotubes (171.4 mg) were then dispersed in 100 mL of deionized water. The mixed solutions were transferred into a beaker to reduce metal precursors and in order to deposit the PdAg nanoparticles onto the surface of the CNT. The final product was washed with an additional 1 L of deionized water, collected by vacuum filtration, and dried overnight in a vacuum oven at room temperature. Pd/CNT and Ag/CNT were synthesized via a method similar to that used for PdAg/CNT. The surface morphologies of the commercial PTFE thin films were studied using a scanning electron microscope (SEM, model JEOL JSM-840A). The sample surface was coated with iridium powder under vacuum before the morphology of the PTFE thin films was investigated. The structure and morphology of the as-prepared PdAg/CNT catalysts were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD analysis of PdAg/CNT catalyst was performed on a Scintag XDS-2000 θ/θ diffractometer (Cu Kα radiation (λ=1.5406 Å)) with 35 mA filament current and 45 kV tube voltage at a continuous scan rate of 1.2 degrees per minute. The mean crystallite size of PdAg/CNT was calculated using the (220) peak based on a combination of Bragg’s law and the relationship between lattice and crystal-lattice spacing given by
\[ L = \frac{0.9 \lambda_{K\alpha}}{B_2 \theta \cos \theta_{\text{max}}} \]

where \( L \) is the mean crystallite size, \( \lambda_{K\alpha} \) is the X-ray wavelength (1.5406 Å), \( B \) is the full width of the peak (rad) at half-maximum (FWHM), and \( \theta_{\text{max}} \) is the Bragg angle (rad) of (220) peak position. TEM images of PdAg/CNT catalysts were collected on a JEOL JEM-4000FX with an operating voltage of 200 kV.

6.3.3 Half-cell tests

Half-cell tests were performed using a conventional three-electrode setup (AFCELL3, Pine Instrument), equipped with a glassy carbon working electrode (AFE3T050GC, Pine Instrument), a Hg/HgO reference electrode (MMO, CHI152, CH Instruments), and a platinum wire counter electrode (AFCTR1, Pine Instrument). All potentials in the present study were referred to MMO-(1.0 M KOH, 0.098 V vs. SHE). 2.0 mg of the as-prepared catalyst was dispersed in 1.0 mL 1-propanol by sonication to form a uniform ink. The working electrode was prepared by drop-casting 10 µL, 20 µL, and 10 µL of ink for Pd/CNT, PdAg/CNT, and Ag/CNT onto the glassy carbon electrode. 10 µL of 0.05 wt% AS-4 ionomer solution (Tokuyama, Inc) was added on top to affix the catalyst particles. Prior to testing, all the electrolytes were de-aerated by purging with high purity \( \text{N}_2 \) for 30 min at ambient temperature. Ten cycles of cyclic voltammograms (CVs) were recorded for each catalyst at a constant sweep rate of 50 mV s\(^{-1}\) in 1.0 M KOH + 0.1 glycerol.

6.3.4 DGFC with PTFE thin film separator

Fuel cell tests were performed on a Scribner Fuel Cell System 850e (Scribner Associates) [48-50]. The membrane electrode assembly (MEA), had an active area of 5 cm\(^2\).
consisting of an anode electrode, a PTFE thin film separator (pore size 0.22, 0.45 or 1.0 µm), a cathode electrode and a carbon paper. The anode electrode was created by air-brushing catalyst ink of 1 mg cm\(^{-2}\) PdAg/CNT with a binder ratio of 9:1 5% polytetrafluoroethylene (PTFE) solution onto an untreated carbon cloth liquid diffusion layer. The cathode electrode was prepared by spraying 3 mg cm\(^{-2}\) Acta 4020 (Fe-based catalyst) with 7:3 ratio of AS-4 ionomer onto PTFE thin film. The dispersion of the ink was mainly controlled by the catalyst ink formulation process in which adequate sonication is normally applied. The surroundings of the PTFE thin film area were sprayed with 100 mL of AS-4 ionomer. Liquid fuel was pumped into the anode compartment at a flow rate of 4.0 ml min\(^{-1}\), while high purity O\(_2\) was fed into the cathode compartment at a flow rate of 200 ml min\(^{-1}\) under a backpressure of 0 psig.

6.3.5 Durability test

The durability of the fuel cell was tested for 80 h at 80°\(^\circ\)C by recording the transient voltage at a constant current density (50 mA cm\(^{-2}\)) discharge. Pure oxygen (99.9%) without humidification at ambient pressure was applied to the cathode compartment at a flow rate of 100 ml min\(^{-1}\). The anode was fed through an open loop by a peristaltic pump with an aqueous solution containing 6.0 M KOH + 1.0 M glycerol at a flow rate of 1.0 ml min\(^{-1}\). To test the variation in polarization curves with the discharge time, the stop/restart procedure was carried out at time points of 20, 40, 60, and 80 h to collect the voltage. After each 20 h, the durability tests were repeated, using fresh fuel each time.
6.3.6 Internal Resistance Measurements and ohmically correct cell voltage ($E_{iR-free}$)

The cell internal resistance was measured by the d.c.-pulse method. The ohmically corrected cell voltage, $E_{iR-free}$, can be determined directly from the experimental data using Equation [1]

$$E_{iR-free} = E_{cell} + \Delta E_{ohmic} = E_{cell} + iR\Omega$$  \[1\]

where $\Delta E_{ohmic}$ (the ohmic voltage loss) can be measured directly via either current-interrupt resistance measurements, and $E_{cell}$ is the cell voltage.

6.4 Results & discussion
6.4.1 Morphology of PTFE thin film or characteristics of the PTFE thin films

Fig. 6.1 shows the SEM images of the surface of the three kinds of porous PTFE thin films. Pore sizes and thicknesses were provided by the manufacturer. It can be seen that there are fibrils and knots in the thin film, with enclosed micropores located among both fibers and knots. The morphology of porous PTFE thin films usually consists of separated phases with solid nodes and fibrils due to agglomeration of the PTFE material and fine threads between the nodes [51, 52]. It can be observed that the PTFE with pore size of 0.22 µm had many small pores densely interconnected with one another, while for PTFE with 0.45 µm pore size most of the pores are lightly interconnected. However, a PTFE with pore size of 1.0 µm leaves large areas not tightly interconnected, knots not uniformly distributed, and the fibrils are weakly oriented. Fig. 6.2 shows the MEA of PTFE thin film (a) and A901 AEM (b), and uniform catalyst layers have been obtained on both PTFE thin film and A901 membrane.
Fig. 6.1 SEM images of different PTFE thin films (a) 0.22 µm, (b) 0.45 µm, and (c) 1.0 µm.

Fig. 6.2 Photographs of sprayed catalysts on (a) PTFE thin film and (b) A901 AEM.
6.4.2 Electrocatalytic study of Pd/CNT, Ag/CNT, and PdAg/CNT in half-cell

As demonstrated in our previous work [28], PdAg/CNT can serve as a better catalyst than Pd/CNT and Ag/CNT for electro-catalytic oxidation of glycerol in a single DGFC setup. Current density and onset potential are the two parameters used to properly evaluate the activity of the catalyst towards glycerol oxidation. Fig. 6.3 shows the CV profiles of glycerol oxidation in N\textsubscript{2} saturated 1.0 M KOH + 0.1 M glycerol on Pd/CNT, PdAg/CNT, and Ag/CNT catalysts at 25\degree C in half-cell setting. The results show that the bimetallic PdAg/CNT catalyst exhibited higher current density (43.4 mA cm\textsuperscript{-2} at 0.16 V) than monometallic Pd/CNT and Ag/CNT catalysts. Furthermore, PdAg/CNT exhibited a more negative onset potential (-0.47 V) compared to those of Pd/CNT (-0.33 V), and Ag/CNT (-0.08 V). Although, Ag/CNT catalyst displayed very little to no activity toward electro-catalytic glycerol oxidation. Alloying Ag and Pd together raised the catalytic activity toward glycerol oxidation and in addition reduced the particle size from 12.9 nm (Ag/CNT) to 2.9 nm (PdAg/CNT).
Fig.6.3 Cyclic Voltammograms of glycerol oxidation reaction on Pd/CNT, PdAg/CNT, and Ag/CNT catalysts in 1.0 M KOH + 1.0 M glycerol, 50 mV s\(^{-1}\), 25°C.

6.4.3 Effect of pore size on PTFE thin film in DGFC

To evaluate the performance of the PTFE thin film-based DGFC, three different PTFE thin films pore sizes were used to prepare MEAs. Fig. 6.4 displays the cell polarization and power density curves of DGFC with PTFE thin film separators using PdAg/CNT as the anode catalyst and a commercial Fe-based cathode catalyst at 80°C. The experiments were performed using three different PTFE thin film pore sizes in an aqueous solution of 6.0 M KOH + 1.0 M glycerol. The open circuit voltage (OCV) of DGFC with PTFE thin film separator with 0.22 µm pore size PTFE thin film was 0.87 V, which is 0.06 V higher than that using 0.45 µm pore size PTFE thin film, and 0.08 V higher than that using 1.0 µm pore size PTFE thin film. As the pore size of PTFE thin film increases, OCV drops due to an increase in fuel crossover from larger pores. Although glycerol can crossover from the anode
through the PTFE thin film separator to the cathode catalyst layer (CCL), the reaction of glycerol with oxygen is slow in the CCL and does not cause notable parasitic overpotential because of presence of non-Pt catalysts that are not catalytically active to glycerol oxidation at the cathode. In typical PEM-DAFCs, in addition to electrochemical reactions of alcohol oxidation on the anode and oxygen reduction on the cathode, the alcohol permeated from the anode to the cathode also reacts directly with oxygen on the cathode noble metal catalyst. The peak power density (PPD) of DGFC with PTFE thin film pore size of 1.0 $\mu$m was 129.9 mW cm$^{-2}$, 15.1% higher than that with PTFE thin film pore size of 0.45 $\mu$m, and 46.9% higher than that with PTFE thin film pore size of 0.22 $\mu$m. The internal resistance (IR) of DGFC with PTFE thin film with 0.22 $\mu$m pore size was 87.5 mOhm, which is 55.3% higher than that with 0.45 $\mu$m pore size PTFE thin film, and 62.9% higher than that with 1.0 $\mu$m pore size PTFE thin film. The performance improvement in the present study can be attributed to the effect of pore size of the PTFE thin film separator. In typical AEM-DAFCs, as $\text{K}^+$ ions do not migrate to the cathode due to only anions selectivity crossing AEM, while in DGFC with PTFE thin film separator, $\text{K}^+$ ions can migrate through the PTFE thin film to the cathode electrode. The PTFE thin film separator allows anions and cations, including both $\text{OH}^-$ and $\text{K}^+$, to freely cross. In this situation, it is necessary for cathode catalysts to have excellent tolerance to the poison of glycerol and good stability in high alkaline solution. The cathode catalyst is a Fe-based macrocycle catalysts (ACTA 4020), used in this study has been proven to be stable enough in alkaline solution, in terms the cathode Fe-based catalyst does not surface-poisoned by $\text{K}^+$ and glycerol. It is known that strong adsorbed anions, such as $\text{SO}_4^{2-}$, $\text{HSO}_4^-$, can chemically adsorbed on noble metal surface (e.g., Pt and Pd) and decrease its electrocatalytic activity. Cations, such as $\text{Na}^+$, $\text{K}^+$ will not chemical
adsorbed on the noble metal surface to influence glycerol electro-oxidation reaction. Indeed, with the base concentration increasing (to some extent), the glycerol electro-oxidation activity increases, it is mainly due to the protonation of glycerol relies on OH\(^-\), it is called base catalysis [53], while from the other point of view, the increasing of cations (K\(^+\) or Na\(^+\)) with base concentration increasing does not counter its activity enhancement. The traditional role of an AEM is to provide a conductive path for the OH\(^-\) ion migration and to prevent the crossover. While crossover of the fuel to the cathode is a general issue, proper modification of MEA can provide the solution to the crossover problem. In addition, the hydrophilic nature of the PTFE separator provides a smaller hydraulic liquid pressure in the cathode, enabling a reduction in water crossover and hence alleviation of cell performance. In summary, the large pore size of PTFE thin film (1.0 \(\mu\)m) enhances diffusion of the charge carriers (OH\(^-\)) transport process to maximize the fuel cell performance.

6.4.4 Effect of PTFE thin film thickness in DGFC

The thicknesses of PTFE thin films with pore size 0.22, 0.45, and 1.0 \(\mu\)m were 210, 215, and 225 \(\mu\)m, respectively. In principle, a thinner film layer reduces the transport time of a charge carrier and thus decreases its ohmic resistance. However, a thinner film layer may display higher fuel crossover that may consequently lead to a loss in fuel cell performance [54]. An appropriate thickness of PTFE thin film can alleviate water flooding and reduce water crossover, so it is essential to find the optimal thickness of the PTFE thin films with respect to design, flexibility, and maximization of cell performance. The results demonstrate that the peak power density increased from 69.0 to 129.9 mW cm\(^-2\) as the thickness of the PTFE thin film increased from 210 to 225 \(\mu\)m; this behavior was due to low
fuel crossover with a thicker film layer and can be attributed to the thick separator, providing more flow resistance between anode and cathode.

Fig. 6.4 Polarization and power density curves of DGFC for different pore sizes of PTFE thin films (0.22, 0.45, 1.0 µm). Anode: PdAg/CNT (20 wt%), 1.0 mg \text{pdag} cm^{-2}, 6.0 M KOH + 1.0 M glycerol, 4.0 ml min^{-1}. Cathode: 4020 Acta, 3.0 mg cm^{-2}, O₂, 200 sccm.

6.4.5 Effect of temperature on PTFE thin film in DGFC

Fig. 6.5 shows the cell polarization and power density curves of DGFC with 1.0 µm pore size PTFE thin film operated at different temperatures. It can be observed that cell performance increases with operating temperatures. An increase in temperature enhances the electrochemical kinetics of both glycerol oxidation reactions at the anode and oxygen reduction reaction (ORR) at the cathode. The OCVs of DGFC operating at 25, 40, 60, and 80°C were 0.65, 0.68, 0.74, and 0.79V, while the PPDs were 18.4, 42.8, 83.9, and 129.9 mW cm⁻², respectively. The conductivity of the hydroxyl ions increases with increasing temperature, reducing the ohmic loss. It is obvious that cell resistance is decreased as the temperature is increased and as a result the cell performance is improved. A higher
temperature improves the glycerol oxidation kinetics, leading to higher fuel cell output power density. Furthermore, both glycerol and oxygen transport diffusivities are increased with an increase in temperature, resulting in low mass transport polarization. PTFE thin films have proven to have excellent endurance in alkaline media and are chemically/thermally stable [55]. The cell performance increases as the temperature is increased; this can be attributed to the faster electrochemical kinetics and increased conductivity of hydroxyl ions and of reactant and products.

Fig. 6.5 Polarization and power density curves of DGFC at different temperatures. Anode: PdAg/CNT (20 wt%), 1.0 mg$_{\text{PdAg}}$ cm$^{-2}$, 6.0 M KOH + 1.0 M glycerol, 4.0 ml min$^{-1}$. Cathode: 4020 Acta, 3.0 mg cm$^{-2}$, O$_2$, 200 sccm, ambient pressure.

6.4.6 Performance comparison of AEM and PTFE thin film in DGFCs

The performances of DGFC employing the PTFE thin film (pore size: 0.45 µm, thickness 215 µm) and A901 AEM (no pore, thickness: 10 µm) under optimized conditions were investigated. In our earlier work [6, 22], various concentrations of KOH and anode fuel
were investigated, and it was found that 6.0 M KOH + 3.0 M fuel concentration produced the highest peak power density [6]. Therefore, in subsequent experiments 6.0 M KOH + 3.0 M glycerol was selected as the optimal fuel. Fig.6.6 illustrates the cell polarization and power density curves of DGFCs with PTFE thin film and A901 AEM using PdAg/CNT as the anode catalyst at 80°C. It can be observed that the OCV of porous PTFE thin film-DGFC is 0.88 V, which is 0.02 V higher than that for A901 AEM. Our previous pore size effect test has demonstrated that the pore size distribution of the thin film is a critical parameter for maximizing fuel cell performance because of its effect on the transport process diffusion of charge carriers (OH⁻). The internal resistance of A901 AEM in DGFC was 11.5 mOhm, which is half of that when using porous PTFE thin films. It can be clearly observed that, as the internal resistance is decreased, cell performance is improved. The PPD of DGFC with A901 AEM is 277.7 mW cm⁻² which is 22.6% higher than the PPD of the porous PTFE thin film (0.45 µm). The practical ohmic losses are due to both electronic contact resistance between the flow fields and the diffusion media as well as the ohmic resistance due to hydroxyl ions conducting through the membrane or the substrate [56]. Therefore, the ohmically-corrected cell voltage, E_{iR-free}, can be determined directly from the experimental data.

The IR-free corrected curves for DGFC with PTFE thin film separator and Anion-exchange membrane were plotted using Equation [1], as shown in Fig. 6.7. The factors contributing to the ohmic losses are the membrane’s ionic conductivity, the membrane thickness (10 µm vs. 215 µm), the electrolyte conductivity, and the catalyst resistance layer. It is clearly noticeable that cell performance of DGFC with PTFE thin film and AEM based DGFC has significantly improved by reducing the ohmic loss. This should guide the future
design of PTFE thin film separators to be small in resistance, so as to generate higher fuel cell power density. Furthermore, while modifying and developing the porous PTFE thin films could demonstrate the feasibility of replacing the large-scale ion-exchange membranes. However, the anticipated drawbacks of using PTFE thin films are that fuel and oxidant species would undesirably be affected by allowing cross reactions. Choosing more appropriate catalysts can be an alternative approach to this problem. In our system, Fe-based cathode catalyst (4020 Acta) has relatively mild catalytic activity towards glycerol oxidation during crossover.

Fig. 6.6 Polarization and power density curves of DGFC with A901 AEM and PTFE thin film (0.45 µm). Anode: PdAg/CNT, 1.0 mg pdag cm⁻², 6.0 M KOH + 3.0 M glycerol; 4.0 ml min⁻¹. Cathode: 4020 Acta, 3.0 mg cm⁻², O₂, 200 sccm, 80°C.
Fig. 6.7 Polarization and power density curves of DGFC with iR-corrected for PTFE thin film. Anode: PdAg/CNT, 1.0 mg\textsubscript{PdAg} cm\textsuperscript{-2}, 6.0 M KOH + 3.0 M glycerol; 4.0 ml min\textsuperscript{-1}. Cathode: 4020 Acta, 3.0 mg cm\textsuperscript{-2}, O\textsubscript{2}, 200 sccm, 80\textdegree}C.

6.4.7 Primary Cost Analysis

The cost of noble metal catalysts and membranes is the main factor for limiting fuel cell commercialization. The cost of the porous PTFE thin films used in our work is ~$8.06 m\textsuperscript{-2}. Commercially available anion-exchange membranes (A901) had a cost of ~ $992.1 m\textsuperscript{-2} (based on small quantity manufacturing cost). Supposing that a 6 x 7 cm area per MEA is needed, PTFE thin film would cost ~ $0.04 per MEA, obviously much less than an A901 AEM that costs ~ $4.31 per MEA. An estimate based on the price of PTFE thin films and AEMs shows that PTFE thin films cost substantially less when compared with A901 AEMs. It should be noted that economy of scale may bring about a cost reduction in the anion exchange membrane Tokuyama A901. From a fuel cell technology viewpoint, an essential development strategy would be to reduce the costs of fuel cell components. Furthermore,
techno-economic analysis could provide economic indicators for use of future alternative PTFE thin films in fuel cell technologies.

6.4.8 Cell voltage degradation for AEM and PTFE thin film in DGFCs

A durability test was used to evaluate the endurance of PTFE thin films and A901 AEMs for DGFC. Fig.6.8 shows results from the 80 h durability test of DGFC with A901 AEM and PTFE thin film at a constant density of 50 mA cm\(^{-2}\) at 80°C. It is interesting to observe that the initial voltage for a PTFE thin film DGFC is about 110 mV higher than that for an AEM-DGFC (0.61 V vs. 0.50 V), suggesting that the steady-state operational performance of PTFE thin film DGFC is better than that of AEM-DGFC. It can be observed that the absolute voltage of both the A901 AEM and the PTFE thin film dropped remarkably after an operational time of about 80 h. The cell voltage decreased with the discharge time, i.e., a 5.8% drop for PTFE thin film and 11.1% drop in cell voltage for A901 AEM over a test period of 80 h. Similarly, the degradation rate of the cell voltage decreased from 1.2 mV h\(^{-1}\) to 0.8 mV h\(^{-1}\) for PTFE thin film, and for the A901 AEM from 9.6 mV h\(^{-1}\) to 3.0 mV h\(^{-1}\) over the 80h period. The cell voltage decreased with time but was partially recovered after each interruption (20, 40, 60, and 80 h), caused by the stop/restart procedure. Such fuel cell degradation can be either reversible or irreversible degradations [57]. The possible voltage that could be recovered by the stop/restart procedure was defined to be reversible degradation, while, the voltage that could not be recovered by the stop/restart procedure was defined to be irreversible degradation [58]. The irreversible degradation loss might be triggered by a change in the microstructure of the catalyst due to agglomeration, dissolution of catalysts, or inactivity of active sites due to fuel crossover. The origin of reversible degradation loss is due to elimination of the hydrophobic property of gas diffusion layer used
on the cathode electrode that results in flooding of MEA; this could be alleviated by changing the airflow rate. KOH in the fuel solution enhances the ionic conductivity of the membrane, producing in the porous PTFE thin film the features of an alkali-doped polymer membrane [18]. The drop in cell voltage and degradation rate percentage is much higher for DGFC with A901 AEM than for PTFE thin film. This demonstrates that PTFE thin films have better endurance than A901 AEM in DGFCs.

![Cell Voltage Curves](image)

Fig.6.8 Transient cell voltage curves at constant current density of 50 mA cm$^{-2}$ over 80 h period of DGFC. Anode: PdAg/CNT, 1.0 mg$_{pdag}$ cm$^{-2}$, 6.0 M KOH + 1.0 M glycerol, 1.0 ml min$^{-1}$. Cathode: 4020 Acta, 3.0 mg cm$^{-2}$, O$_2$, 100 sccm, ambient pressure, 80°C.

6.4.9 Electrode degradation on anode

Fig. 6.9 shows the TEM images and the corresponding metal particle size histograms of PdAg particles supported on CNT both before and after the durability test. The bimetallic PdAg nanoparticles are well dispersed on CNT with uniform particle size distribution. The average particle size, determined by randomly measuring 100 particles, was 2.9 nm. The
particle size distributions are fairly narrow, ranging from 2.2 to 3.8 nm for PdAg before the durability test and 2.4 to 5.0 nm for PdAg after the durability test. The TEM results show that the average particle size of the anode catalyst increases from 2.9 nm to 3.7 nm after the durability test, reducing the electrochemically active surface area and hence causing a decrease in anode performance. A small amount of agglomerations of PdAg particles appear on the CNT support while individual PdAg particles have also grown, broadening the average particle size to 3.7 nm. The growth caused by the random cluster-cluster collisions accompanied by liquid-like coalescence of the particles may contribute to the agglomeration and growth of the catalyst particles [59]. XRD patterns for PdAg/CNT catalyst before and after the durability test are shown in Fig. 6.10. The peak of 25°, which is the wide graphite (002) peak, suggests that CNT support has a good graphite characteristic. It can be observed that there is no further peak shift (111, 200, 220, and 311) of PdAg/CNT before and after the durability test. The mean crystal size values calculated using the Debye-Scherrer formula were 2.9 nm and 3.6 nm, respectively, for PdAg/CNT before and after the durability test, in good agreement with the TEM results. It could therefore be logically concluded that PdAg/CNT remains alloyed and crystalline after the 80h durability interval. We proposed that the decrease in the cell voltage after long-term discharge is mainly attributable to the loss of the anode performance.
Fig. 6.9 TEM images of PdAg/CNT before (a) and after (b) the durability test.

Fig. 6.10 XRD image of PdAg/CNT before and after the durability test.
6.4.10 Future outlook

It is important to develop a strategy for reducing the cost of direct alcohol fuel cell components for their widespread applications. AEM-DAFCs have attracted enormous attention, however, the critical issues of AEM cost and durability need to overcome. In general, a high concentration alkaline solution is desired to get a high OH⁻ conductivity, and development of AEMs adequate for high OH⁻ conductivity with low alkaline feed solutions is highly demanded particularly considering the undesired AEM durability in concentrated base solution. Therefore, development of low cost, alkali-tolerant PTFE thin film separator based alkaline DAFC technologies are promising to replace AEMs. A big advantage is that the anion conductivity is not limited by AEM. The state-of-art of AEM (Tokoyama) is <0.1 S/cm [60], while the anion conductivity of a 0.125 M NaOH solution is 0.206 S/cm [61]. Since the PTFE itself is much chemically robust in high concentration alkaline solution, therefore, higher concentration liquid base can be used (e.g., 6.0 M NaOH), and it has much higher than anion conductivity than an AEM, to reduce the internal resistance and improve mass/charge transfer for a DAFC. Further, such porous PTFE thin film has cost advantage compared to AEM. Searching for cost-effective stable anode catalysts is another important directions for future research in fuel cell technologies. Currently supported noble metal (such as Pt, Pd) nanoparticles, still serve as anode catalysts, reduction in noble metal loading by optimizing the anode structure and developing more efficient electrode and catalyst support materials is one research direction, exploration of non-noble metal catalysts for alcohol oxidation at high pH media is the other one. There are still many open questions that must be answered before successful commercialization of porous PTFE thin film separator in fuel
cells. Optimization and search for new systems will lead to new development and possibly to practical deployment of PTFE thin films for direct alcohol fuel cell technologies.

6.5 Conclusions

In the present work, DGFC was developed using a porous PTFE thin film as a separator of fuel and oxidant streams. The electrocatalytic activities of Pd/CNT, PdAg/CNT, and Ag/CNT on glycerol oxidation, identified by cyclic voltammetry, showed that PdAg/CNT produces the highest current density. DGFCs using PTFE thin film with PdAg/CNT anode catalyst and Fe-based cathode catalyst achieved a maximum peak power density of 214.7 mW cm$^{-2}$ at 80°C. Three porous PTFE films of different pore sizes and thicknesses were studied to seek understanding of the link between pore size and cell performance. The pore size effect of PTFE thin film separator showed that a larger thin film pore size of 1.0 µm enhanced diffusion in the charge carriers (OH$^-$) transport process to maximize fuel cell performance. The performance of DGFCs employed with PTFE thin film and A901 AEM was investigated for comparison. Although the real performance of the DGFC employed with PTFE thin film is 22.6% lower than that of A901 AEM-based DGFC, IR-corrected polarization curves of the PTFE thin film DGFC suggest that fuel cell performances are indeed very close after removing internal resistance. Considering the thickness, PTFE thin film (215 µm) raises twice internal resistance than A901 AEM (10 µm), future PTFE thin film research should be focused on optimizing thickness, pore structure, and hydrophobicity to reduce fuel cell’s internal resistance, thus improving the overall fuel cell performance. The 80 h durability test indicated that the major voltage loss occurs during the initial discharge stage, but the loss becomes smaller and more stable with discharge time. We report a 5.8% decrease in cell voltage for PTFE thin film DGFC and an
11.1% decrease in cell voltage for A901 AEM-DGFC; the degradation rate of cell voltage over the 80 h period similarly decreases from 1.2 mV h$^{-1}$ to 0.8 mV h$^{-1}$ for PTFE thin film, and for A901 AEM from 9.6 mV h$^{-1}$ to 3.0 mV h$^{-1}$. The voltage loss is mainly caused by performance reduction at the anode due to both the agglomeration and the growth of the catalyst particles from 2.9 to 3.7 nm. Using DGFCs with PTFE thin films separator without further synthesizing or modification, these films in this work breaks the paradigm and demonstrates a PTFE thin film separator capable of operating with lower ionic resistance than benchmark state-of-the-art anion exchange membranes.

6.6 Acknowledgements

We acknowledge financial support from the US National Science Foundation (CBET-1159448, 1501124) and the Iowa State University startup fund. The authors are grateful to Darcie H. Farrell and Qi Liu of Iowa State University for assistance in fuel cell experiments.

6.7 References


The use of selective ion-exchange membranes, metal catalysts, and high-purity fuels in the fuel cell systems raises concerns about the overall cost of fuel cells. Here, we integrated a carbon-based cathode catalyst (N-S-doped mesoporous carbon CMK-3), inexpensive and durable porous thin film separator (PTFE), and crude biorenewable fuels such as crude glycerol (88.8%), bio-oil into fuel cells to generate low cost bio-electricity to demonstrate a promise toward the development of novel alkaline fuel cells with high performance, low cost, and desired durability. My preliminary results are shown in Fig 7.1 and Fig. 7.2. The peak power density of a fuel cell with 30 wt% crude glycerol (88.8%, 2.86M) fuel is 62 mW/cm², which is 80% of that with 3.0 M high-purity glycerol (99.9%) fuel, while the peak power density of a fuel cell with crude bio-oil (30 wt%) reaches 16 mW/cm². This work opens opportunities for developing inexpensive direct crude biomass fuel cell technologies. Further optimization and systematical search for new catalytic and separator materials with low cost and high durability may lead to new development and possibly practical deployment of direct alcohol fuel cells.

*The material contained in this chapter was submitted for a U.S Patent on March 14, 2007. Low cost and high performance fuel cells fed with biomass-derived feedstock by Wenzhen Li, Neeva Benipal, Yang Qiu, Ji Qi.
Fig. 7.1 Polarization and power density curves of directly crude biomass fed fuel cell anode: PdAg/CNT (20 wt%), 1.0 mg_{PdAg} cm^{-2}, PTFE substrate (1.0 µm), 6.0 M KOH + 30 wt% crude glycerol or 3.0 M glycerol cathode: N-S-CMK-3, 2.0 mg cm^{-2}, 200 sccm O_2.

Fig. 7.2 Polarization and power density curves of direct crude biomass fed fuel cell, anode: PdAg/CNT, PTFE substrate (1.0 µm), 1.0 mg_{PdAg} cm^{-2}, 6.0 M KOH + 30 wt% bio-oil, 6.0 M KOH + 30 wt% crude glycerol; cathode: N-S-CMK-3, 2.0 mg cm^{-2}, O_2.
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†: equal contribution author, *: corresponding author

Patents

- Wenzhen Li, **Neeva Benipal**, Yang Qiu, Ji Qi, *Low cost and high performance fuel cells fed with biomass-derived feedstock*, US patent to be submitted on March 14, 2017.