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Electrocatalysts design for selective oxidation of organic molecules in high-performance fuel cell

Ji Qi
Iowa State University

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Electrocatalysts design for selective oxidation of organic molecules
in high-performance fuel cell

by

Ji Qi

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

Major: Chemical Engineering

Program of Study Committee:
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Brent H. Shanks
Jean-Philippe Tessonnier
Wenyu Huang

Iowa State University
Ames, Iowa

2016

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DEDICATION

I dedicate this dissertation to the history of human. I wish one day human can fully understand the essence of nature.
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<tr>
<td>ADOR</td>
<td>Aldehyde oxidation reaction</td>
</tr>
<tr>
<td>AEM</td>
<td>Anion exchange membrane</td>
</tr>
<tr>
<td>AEMFC</td>
<td>Anion-exchange membrane fuel cell</td>
</tr>
<tr>
<td>AFC</td>
<td>Alkaline fuel cell</td>
</tr>
<tr>
<td>AOR</td>
<td>Alcohol oxidation reaction</td>
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<td>CA</td>
<td>Chronoamperometry</td>
</tr>
<tr>
<td>CCM</td>
<td>Catalyst coated membrane</td>
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<td>CNT</td>
<td>Carbon nanotube</td>
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<td>Cyclic voltammogram</td>
</tr>
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<td>Direct alcohol fuel cell</td>
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<td>Direct ethanol fuel cell</td>
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<td>Direct glycerol fuel cell</td>
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<tr>
<td>GOR</td>
<td>Glycerol oxidation reaction</td>
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<td>HPLC</td>
<td>High performance liquid chromatography</td>
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<tr>
<td>HSAB</td>
<td>Hard soft acids and bases</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
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<tr>
<td>LSV</td>
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<tr>
<td>RHE</td>
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<td>RID</td>
<td>Refractive index detector</td>
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<tr>
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<td>Surface dealloyed</td>
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<td>Scanning electron microscopy</td>
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<td>SOFC</td>
<td>Solid oxide fuel cell</td>
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<td>X-ray diffraction</td>
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ABSTRACT

In the long run, electrocatalysts should be rationally designed instead of being developed by random trial and error approaches. The present Ph.D. research work is to push forward toward this ultimate goal by establishing some detailed strategies of electrocatalysts design for selective oxidation of organic molecules such as alcohols (methanol, ethanol, ethylene glycol, and glycerol), aldehydes (formaldehyde, acetaldehyde, glycolaldehyde, glyceraldehyde and glyoxylate), and carbohydrazide, for fuel cell applications.

The first strategy is designing the morphology of catalysts (e.g. roughness, 3D structure) with optimized particle size and dispersion. With surface area increasing, surface dealloyed PtCo nanoparticles supported on carbon nanotube (SD-PtCo/CNT) were prepared by ex-situ method and used for crude glycerol oxidation. SD-PtCo/CNT anode catalyst based AEMFC with a 0.5 mgPt cm\(^{-2}\) achieved peak power densities of 268.5 mW cm\(^{-2}\) (88% crude glycerol/O\(_2\)) and 284.6 mW cm\(^{-2}\) (high purity (99.9%) glycerol/O\(_2\)) at 80 °C and ambient pressure. 3D graphene, a carbon-only catalyst prepared by reduction of carbon monoxide with lithium oxide, is found to electrochemically catalyze carbohydrazide oxidation reaction efficiently. Prototypes of anode metal catalyst free and completely metal catalyst free anion exchange membrane fuel cell with 3D graphene anode catalyst generate peak power density of 75.1 mW cm\(^{-2}\) and 24.9 mW cm\(^{-2}\), respectively. With carbon nanotubes as the anode catalyst (3D catalyst layer), anode metal-catalyst-free and completely metal-catalyst-free direct carbohydrazide anion exchange membrane fuel cells have demonstrated to be able to generate a peak power density of 77.5 mW cm\(^{-2}\) and 26.5 mW cm\(^{-2}\), respectively.
The second strategy is comparing different monometallic catalysts’ activity towards different reaction intermediates through experiments, and rationally combining them to facilitate entire reaction network by taking advantage of the synergetic effect. For electrocatalytic oxidation of glycerol, it is found Pd can re-adsorb the desorbed glycerate in the bulk electrolyte and further oxidize it to tartronate while Au can alleviate C-C bond cleavage of C3 species. Therefore, combining Pd and Au takes advantage of these effects synergistically, maximizing the yield of tartronate in electrocatalytic glycerol oxidation reaction. PdAu alloy also increases glycerol and glycerate reaction rate, so that higher power output and yield of tartronate in shorter reaction time can be achieved in anion exchange membrane fuel cell.

The third strategy is screening elements with quantum theory and calculation for the activity towards certain reaction intermediates. After experimental confirmation of theoretical prediction results, combining the well-defined active sites to obtain the catalyst with maximum activity towards the entire reaction network. Orbital energy difference matching is proposed as a new descriptor for screening electrocatalysts with respect to the charge transfer process, during which the homogeneous reaction can be electrochemically heterogenized with polarized electrocatalytic materials. Combining different catalytic active sites targeting at original substrate or reaction intermediates is proposed as a new strategy of designing multi-functional catalysts to take advantage of spillover effect in heterogeneous catalysis. Herein, electrocatalytic oxidation of aldehyde and alcohol serves as an example, the range of electrocatalyst candidates for intermediate aldehyde oxidation was firstly narrowed to Lewis soft acids via hard and soft acids and bases (HSAB) theory from an adsorption aspect, followed by targeting at Ag, Au and Pd with the descriptor of orbital energy difference matching from a charge transfer aspect. After confirming the high electrocatalytic activity of Ag towards
aldehyde (formaldehyde, acetaldehyde and glyoxylate) oxidation with cyclic voltammetry, Pd for hydroxyl group deprotonation and Ag for aldehyde intermediates oxidation were combined for the highest activity towards the whole alcohol oxidation reaction network. The bimetallic PdAg supported on carbon nanotube (PdAg/CNT) was prepared via a wet-chemistry method, and then applied as a highly active anode catalyst (0.5 mg Pd cm$^{-2}$) for direct alcohol fuel cells (DAFCs) with peak power densities of 135.1 mW cm$^{-2}$, 202.3 mW cm$^{-2}$, 245.2 mW cm$^{-2}$, 276.2 mW cm$^{-2}$ when using methanol, ethanol, ethylene glycol and glycerol as fuel respectively, which are much higher than monometallic Pd anode catalyst-based DAFCs.
CHAPTER 1 INTRODUCTION

1.1 Objectives of the Research:

With the world population growing, easy-reaching petroleum reserve declining and environmental pressure increasing, sustainably meeting humanity's increasing energy needs has been identified as the top challenge in next decades. Recently, more and more electricity has been generated from renewable sources, such as solar panels and wind turbines, and need to be either stored for later peak-hour use or utilized to produce chemicals, polymers or fuels. Electrocatalysis (widely employed in fuel cells and electrolyzers) technology, will play a more important role in our future sustainable energy, chemicals and materials landscape. After a long time random trial and error at lab scale and massively systematic screening [1], rational design of electrocatalysts combining modern experimental tools and advanced theory have become inevitable to shorten the industrialization period of catalysts and lower their development cost. Many catalytic reactions involving organic molecules, which are critical transformations in sustainable energy and green chemistry, involve the coupling or cleavage of a bond between carbon (C), nitrogen (N), hydrogen (H) and oxygen (O). To oxidize organic compounds containing carbon atoms to target products, the major tasks are to selectively cleave or protect O-H, C-C, C-H, and C-N bonds, etc.

The objectives of my Ph.D. dissertation are (1) study efficient electrocatalysts for selective oxidation of organic molecules in the fuel cell reactors to cogenerate electricity
and target products (2) make primary efforts on incorporating of theoretical quantum chemistry to assist the rational electrocatalysts design.

1.2 A Review of the State of the Art Knowledge in the Area:

1.2.1 Target and method of catalyst design

Petroleum-based refinery has dominated the industrial chemistry in the 20th century and early 21st century. However, our heavy reliance on exported oil and the fluctuation of oil cost - for example, the barrel price of oil once roared up to a peak value of 145 US$ in June, 2008- is becoming an obstacle towards a stable economy. Since the crude oil reserve is limited, the petroleum-based refinery is unsustainable in the long run. Diversifying our energy sources is critically important towards a sustainable future. 1 % of incoming sunlight is stored by forests and crops into biomass as a renewable feedstock. [2] It is necessary to gradually transform the current petroleum-based refinery to renewable biomass-based refinery to produce the fuels, chemicals and materials.

Novel catalyst design and efficient chemical transformation play key roles in achieving this goal. 90% percent of industrialized catalysts are solid[3]. The solid catalysts have a 15 billion US$ worldwide market sales value per year, which creates an added value about 100-1000 times higher than its own price.[4] Although heterogeneous catalysis process dominated the state of the art, homogeneous catalysts and enzymes have an increasing share in the chemical processes since they require milder reaction condition and are very selective to desired products.[5] In this dissertation, we will focus on the rationale design of solid electrocatalyst as a branch of heterogeneous catalysis for organic molecules conversion.
The ultimate goal of catalyst design is to have profound understanding of factors determining catalytic functions (activity and selectivity) to be able to design and prepare efficient catalysts at the atomic level.[6] Catalyst design can be classified to active site design and morphology design. The active site design is to rationally integrate different elements in their proper chemical state, so that this active site can have designated catalytic functions. This is extremely challenging because different element has different catalytic activity towards different substrates (reactant and reaction intermediates) in the reaction network. To explain the different catalytic ability among different active sites, certain mechanisms based on the mutual function of these active sites have to be understood, taking into account as many theoretical and experimental tools as possible. For instance, the Brønsted–Lowry acid–base theory and Lewis acid–base theory have been contributing to such explanation since the 20th century. Recently, along with the development of computational quantum calculation method (semi-empirical method, density functional theory (DFT), etc.), descriptor based active sites screening has attracted more research attention.[7, 8]

The morphology design is to take advantage of the relationship between surface area and structure of the catalyst and the catalytic functions. For example, porosity of the catalysts can be rationally designed to tune the reactant selectivity, product selectivity and transition state selectivity.[9] The pore size of the catalytic materials affects and restricts the dimensions of individual molecules in the reaction pathway, thus being able to tune the product selectivity.
1.2.2 Electrocatalyst design from massively systematic screening to rationally theoretical screening

Current catalysis technology is still largely relied on “art” rather than “science”. It remains a grand challenge to answer “how we can rationally design an efficient catalyst for an electrochemical reaction” and “it is possible that the best catalyst is hidden for this electrocatalytic reaction? – which is much more efficient than the currently used one”. After a long period of random trial and error lab scale research and development, catalysis researchers have come to realize that massively systematic screening by combinatorial electrochemistry is necessary to find the best catalyst composition.[1] As identifying certain highly active electrocatalysts, quantum chemistry calculations have been performed to explain the catalytic functions and elucidate the reaction pathways at the molecular level, [10-13] taking into account of the applied potential and solvent effects [11, 14-16].

These insights gained finally give birth to density functional theory (DFT) guided catalysts screening towards electrocatalytic transformation of simple molecules such as H₂[17], O₂[18], H₂O[13, 19] in recent years. For example, for hydrogen evolution reaction (water reduction reaction), catalysts have been screened according to the adsorption energy [19] or binding energy [20] of hydrogen onto the metal surface. Similarly, adsorption energy has been also used as a descriptor for catalyst screening for acetylene hydrogenation reaction [21] in the conventional heterogeneous catalytic process. Other descriptors such as activation barrier [17], the position of the d-band center relative to the Fermi level [22] have also played vital roles in theory guided catalyst selection for hydrogen oxidation and oxygen reduction reaction, respectively. These are breakthrough researches since dominant
descriptors influencing the catalytic activity have been used for rational electrocatalyst design.

However, the effective screen of catalyst for electrochemical oxidation or reduction processes cannot only rely on a single descriptor despite of its significance, especially for some complicated reaction networks involving much bigger organic molecules/species as reaction intermediates. Therefore, there is an urgent need to develop new practical electrocatalyst design strategy for more complicated reactions, which may require new theoretical tools to identify other important descriptors, and experimental confirmation methods to determine all the major reaction intermediates and their reactivity over different catalysts.

1.2.3 Selective oxidation of organic molecules in high-performance fuel cell: marrying an electricity generation device with a catalytic reactor

1.2.3.1 General introduction of fuel cell reactor for organic molecules oxidation reaction

Fuel cells have long been regarded mainly as an electrochemical device converting chemical energy (stored in fuels) into electrical energy with an efficiency of 40-50% (not limited by Carnot’s theorem), which is higher than a heat engine. If oxygen-containing organics can be oxidized to some useful products, the anode chamber can be employed as a reactor for the selective oxidation reaction, leading to cogeneration of valuable chemicals and electricity.

During the low-temperature oxidation reaction, ideal electrocatalysts should be able to cleave all the carbon bonds (e.g. C-H, C-C and C-N) except C-O bonds to maximize the
In general, fuel cell can be classified into the following types: Polymer Electrolyte Fuel Cell (PEFC), Phosphoric Acid Fuel Cell (PAFC), Alkaline Fuel Cell (AFC), Molten Carbonate Fuel Cell (MCFC), and Solid Oxide Fuel Cell (SOFC).

As shown in Table 1.1, PEFC differs from other types of fuel cell in the operating temperature and applied fuel. PEFC, which works under low temperature and has a wide range of compatible liquid fuel, has wide applications such as vehicles, portable devices, and other small scale electrical appliances.
Table 1.1 Conventional classification of fuel cell

<table>
<thead>
<tr>
<th></th>
<th>PEFC</th>
<th>PAFC</th>
<th>AFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>PEM (proton</td>
<td>AEM (anion</td>
<td>Liquid H3PO4</td>
<td>Liquid KOH</td>
<td>Molten</td>
</tr>
<tr>
<td></td>
<td>exchange</td>
<td>exchange</td>
<td>(immobilized)</td>
<td>(immobilized)</td>
<td>carbonate</td>
</tr>
<tr>
<td></td>
<td>membrane)</td>
<td>membrane)</td>
<td>d)</td>
<td>d)</td>
<td></td>
</tr>
<tr>
<td>Charge carrier</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>CO₃²⁻</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O²⁻</td>
</tr>
<tr>
<td>Operating</td>
<td>80°C</td>
<td>80°C</td>
<td>200°C</td>
<td>60–220°C</td>
<td>650°C</td>
</tr>
<tr>
<td>temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>600–1000°C</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Platinum</td>
<td>Platinum or</td>
<td>Platinum or</td>
<td>Nickel</td>
<td>Perovskites</td>
</tr>
<tr>
<td></td>
<td></td>
<td>non-precious</td>
<td>non-precious</td>
<td></td>
<td>(ceramic)</td>
</tr>
<tr>
<td></td>
<td>metal</td>
<td>metal</td>
<td>metal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell components</td>
<td>Carbon based</td>
<td>Carbon based</td>
<td>Carbon based</td>
<td>Stainless based</td>
<td>Ceramic based</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>based</td>
<td></td>
</tr>
<tr>
<td>Fuel compatibility</td>
<td>H₂, alcohol</td>
<td>H₂, alcohol</td>
<td>H₂</td>
<td>H₂, CH₄</td>
<td>H₂, CH₄, CO</td>
</tr>
</tbody>
</table>

Compared to other types of fuel cells, AEMFC has several advantages:

1. Aqueous phase solution can be used as feedstock in AEMFC, which broadens the feedstock range of fuel cell, and opens avenues to the electrocatalytic biorefinery. Theoretically, polyols and sugars have higher energy density than hydrogen, offering potential opportunity to get high electrical energy generation performance. Although their electromotive forces (theoretical potentials) are slightly lower than hydrogen, the theoretical energy conversion efficiencies of methanol, ethanol, EG and glycerol are in range of 97% to 99%, that are higher that of hydrogen (83%). The mass and volume energy densities of the alcohols are also higher than that of hydrogen.
2. Due to the difficulty of the C-C bond cleavage at low temperature (e.g. <80°C), biorenewable C2+ compounds cannot be completely oxidized to CO₂ and H₂O to get the highest power output, especially at low temperature and in alkaline electrolyte. However, value-added chemicals can be obtained by partial oxidation, i.e. glycerol or sorbitol oxidation.

3. An advantage of polyhydric alcohols (polyols) as fuel compared to monohydric alcohol (i.e. biorenewable ethanol, butanol) is their high Faradic efficiency. For example, full oxidation of glycerol to mesoxalic acid without C-C bond breaking involves 10 electrons transfer, its Faradic efficiency is 72% as reference to full oxidation product CO₂ (10 e transferred / 14 e⁻ to CO₂), even without considering production of valuable chemicals. The Faradic efficiency is only 30% for partial oxidation of ethanol to acetic acid (4 e⁻ / 12 e⁻ for complete oxidation to CO₂). Higher Faradic efficiency offers a chance to find the balance point between valued product distribution and power output.

4. At the cathode side, relatively cheaper non-platinum catalysts have longer durability and more facile kinetics for oxygen reduction reaction (ORR) in AEMFC than in PEMFC. Therefore, the overall fuel cell (electrochemical reactor) cost can be significantly reduced due to employing inexpensive non-Pt cathode catalysts.

5. As far as the ion exchange membrane is concerned, alkaline electrolyte membrane is cheaper than acid electrolyte membrane (e.g. NafionR). Because solid AEMs have no fixed cations and possess a distinct OH⁻ transfer and diffusion behavior compared to
liquid base solution, they provide a unique alkaline reaction environment for low
temperature electrocatalytic reactions. The rapidly developed AEMs are typically
based on quaternary ammonium hydroxide (QAOH) polymers. The OH⁻ conductivity
of commercial AEMs (e.g. Tokuyama A201) can reach >30 mS/cm.[23] Although the
long-time durability of AEMs need to be greatly improved for a practical application,
the state-of-art AEMs are durable to H₂O₂, and can be operated at 80°C without
chemical/structural changes. Under such low temperature operation, undesirable
decomposition of polyols / sugars does not occur. The AEM's intriguing characteristics
of no mobile cations (e.g. K⁺) alleviates carbonate precipitations that could destroy an
electrolyte, thus greatly minimizing cation-associated issues.[24] The anions crossing
from cathode to anode further reduce alcohol crossover problems, thus improving fuel
cell performance and fuel utilization.

Overall, fuel crossover from anode to cathode is alleviated by the cathode to anode
directional electric osmotic drag, while non-platinum catalysts on the cathode eliminate the
oxidation of the fuel that transported from the anode side, because they are nearly inert to
organic oxidation reaction, therefore, AEMFCs, in principle, avoid 'short-circuit potential'
and improving fuel cell performance.
1.3 Experimental Setup

1.3.1 General synthesis strategy targeted at surfactant free bimetal nanocatalysts with controlled size, shape, tuned electronic properties and optimized surface ensembles

1) Binary precious metal catalysts. Based on previously published references, Pt, Pd, and Au have remarkable performances in electrooxidation of polyols and sugars in high pH. Pt is able to oxidize primary OH and break the C-C bond at low electrode potential to generate high electricity, Pd facilitates OH oxidation, and Au is sluggish to break the C-C bond. The Pt, Pd, Au, alloy nano-structure catalysts, were prepared and are expected to maintain their individual merits to achieve high cogeneration ability.

2) Precious metal non-precious metal catalysts. The choice of non-precious metal will be based on their functions demonstrated in multi-metallic catalysts. For example, Sn was reported to be able to tune electronic properties of precious metals. Bi was found to be able to dilute Pt/Pd surface sites, thus suppressing C-C cleavage. Ni and Zn have unique OH- adsorption properties. In this research, non-precious metal Co serves as a sacrificial metal to generate a high rough surface and tune the lattice parameter of a Pt-based catalyst (surface dealloyed Pt-Co nanoparticles) for glycerol oxidation.

3) Carbon nanotubes (CNTs) have been employed as the catalyst support, because it has been discovered that the unique 1-D morphology and electronic structure of CNT can facilitate electronic conduction path and promote mass transport.
1.3.2 Physical characterization

High-resolution transmission electron microscopy (HRTEM) will be used to observe the shape, size, and size distribution of metallic nanostructures. X-ray diffraction (XRD) will be conducted to determine the average primary crystalline size using the Debye-Scherrer equation. It will also provide information about the alloy degree of a bimetallic catalyst by calculating its lattice parameter. X-photon electron spectroscopy (XPS) will be performed to detect the surface composition and the chemical state of the catalyst. Thermogravimetric analysis (TGA) will ascertain metal loading, surfactant amount and compositions in the catalysts. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) will be used to analyze the bulk composition of multi-metallic catalysts. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) coupled with high-resolution extensive diffraction spectroscopy (HR-EDS) will give surface element mapping. FTIR and Raman spectroscopy combined with probe molecules will be employed to identify catalyst surface compositions. These characterizations will be in collaboration with Dr. Wu at Oak Ridge National Lab.

**XRD**: A Scintag XDS2000 Powder Diffractometer Instrument equipped with Cu K\(_\alpha\) (\(\lambda = 1.5406\) Å) source will be employed to collect X-ray diffraction data for the as-prepared nanostructures. Structure information will be obtained by using the Scintag DMSNT software. The diameter of nanostructures will be calculated by Debye-Scherrer formula:
\[ L = \frac{0.9\lambda_{K\alpha}}{B_{20}\cos\theta_{\text{max}}} \]

And the lattice parameter is calculated by

\[ \alpha_{\text{fcc}} = \frac{\sqrt{2}\lambda_{K\alpha}}{\sin \theta_B} \]

**TEM:** JEOL JEM-4000FX transmission electron microscopy (TEM) will be employed to examine the morphologies and compositions of as-prepared nanostructures. Before tests, the as-prepared catalysts will first be dispersed in ethanol to form a uniform dilute solution, followed by depositing one or two drops of this solution on a carbon film covered copper holder. The average size (length or diameter) and its histogram of the as-prepared samples will be analyzed from the TEM images, by randomly measuring over 100 nanostructures. Also, the surface crystal facet could be investigated in HRTEM by measuring the atom interlayer spacing. The composition will be analyzed by the Energy-dispersive X-ray spectroscopy (EDX) connected to TEM by taking the average of at least five different points from the sample.

**XPS:** X-ray photoelectron spectroscopy (XPS) will be employed to analyze the surface elements composition of as-prepared catalysts. The composition of metal elements will be evaluated by the equation:

\[ X_A = \frac{\sum_{i=A}^{n} \frac{I_i M_i}{S_i}}{\sum_{i=A}^{n} \frac{I_i M_i}{S_i}} \]

Where \( X_i \), \( I_i \), \( M_i \), and \( S_i \), are the molar fraction, measured photoelectron intensity, molar volume, and sensitivity factor of element \( i \).
**ICP-AES**: Inductively coupled plasma - atomic emission spectroscopy (ICP-AES) will be used to analyze the bulk elements composition of as-prepared catalysts. 1mg as-prepared catalysts will be dissolved in 4 ml Aqua Regia, by adding 1ml concentrated nitric acid and 3ml concentrated hydrochloric acid. The solvent will be further diluted to 100ml. The ICP test will give out the weight ratio of the different elements in bulk.

**TGA**: Thermal gravimetric analysis (TGA) will be carried out to analyze the weight percentage of surfactants and the metal loading on as-prepared catalysts. 6-10 mg of the as-prepared catalysts will be heated up to 500°C in an alumina holder under an N₂ gas flow at the rate of 10°C/min. After holding the temperature for 20 min, the N₂ gas will be shifted to air flow and the sample will be heated to 900°C at the same heating rate. Because the main compositions of the as-prepared catalysts are of good thermo stability in inert gas atmosphere, the weight loss at low temperature range under inert gas could be attributed to the decomposition of surfactants. Keep increasing the temperature in an air atmosphere will burn out all the carbon based catalysts supports and giving out the real metal loadings. Also, the temperature dependent weight loss profile will give information of the surfactants decomposition temperature, which could be used to direct the thermo treatment in the experiment.
1.3.3 Half electrolysis cell and onsite-collection-off-site HPLC analysis

![Figure 1.1 a) electrochemical workstation lined with three-compartment-cell and rotating disk electrode (RDE), b) HPLC Agilent 1100 with refractive index detector (RID) and variable wavelength detector (VWD)](image)

**Figure 1.1** a) electrochemical workstation lined with three-compartment-cell and rotating disk electrode (RDE), b) HPLC Agilent 1100 with refractive index detector (RID) and variable wavelength detector (VWD)

Commercial and self-prepared carbon supported mono- and bimetal Pt, Pd, Au, etc catalysts will be studied in half cell. Presented in Figure. 1.2 a), an electrochemical workstation (PAR, VMC-2) with a rotating disk electrode (RDE) and 3-compartment-cell setup (Pine) will be used to study the selective electrooxidation. In Figure. 1.2 b), HPLC Agilent 1100 with RID and VWD will give the product concentrations (in the electrolyte)
for calculating reactant conversion and catalyst selectivity. An HPLC column (OA-1000 Grace or HPX-87H Bio-Rad) will serve for the small organic molecule separation and mass spectrometry (MS) will be employed to identify unknown products (not recorded in the retention-time database). Bimetal catalysts will be deposited on a glassy carbon working electrode or a gas diffusion layer (GDL, mimicking fuel cell electrode) working electrode. The product distribution under applied potential will be investigated in the 3-compartment-cell. A self-designed online sample collection and offline HPLC analysis technique will be used. A long, tiny syringe will be positioned close (0.5 mm) to the working electrode and a peristaltic pump (Miniplus3, Gilson) will be used to take a small dose (50-55 μL) of electrolyte with products for the HPLC analysis. The small electrolyte volume loss will not affect the reactant mass transport and the overall reaction. We will collect product samples at different time periods using slow linear scan (e.g. 1 mV/s) and staircase-increment scan (e.g. 30 s increments for 30 mV staircase) schemes. This method will give accurate product concentrations under different potentials.

The reaction conditions, such as electrolyte pH, reaction temperature, reactant concentration, ratio of reactant to base, ratio of catalyst to reactant, base source (e.g. KOH, NaOH, solid AEM), and stirring speed will be examined to learn their effects on the product distributions. In particular, an anion exchange ionomer (AEI) will be used to cover the catalyst surface to study its OH- transfer/diffusion behavior. Key parameters to controlling different elementary bond breaking and making steps will be identified. The competitive reaction steps in glycerol oxidation include primary and secondary OH oxidation, and C-C cleavage. It is essential to identify the step sequence with increasing applied potential under certain reaction conditions. The 'relationship roadmap' will be constructed with
applied potential (X-axis), generated current (electricity generation, Y-axis), and product distribution (chemical production at given potentials, Z-axis). We will link the electricity and chemical cogeneration behaviors between single AEMFCs and half-cell (electrolysis cell) based on the bimetal catalysts.

1.3.4 Electricity generation in fuel cell with electricity co-generation

Figure 1.2 Scribner Associates model 850e fuel cell test station running open loop test

The self-developed bimetal catalyst and anion exchange ionomer (e.g. Tokoyama, AS-4) will be dispersed in alcohol to form homogeneous ink, and then sprayed on AEM (e.g. Tokoyama, A201) to make a catalyst coated membrane (CCM). The cathode catalyst (e.g. Pt, Au or non-precious metal Ag, FeCo-N/C) layer will be fabricated on the other side of the CCM. A MEA will be finally obtained by pressing a carbon cloth and a carbon paper
as anode and cathode substrates, respectively. The MEA will be assembled into a single fuel cell stack. The serpentine flow channel area is 5.0 \((2.3 \times 2.2)^2\) cm. A Scribner 850e fuel cell test system will be used to collect polarization (I-V) curves. The anode over-potential will be monitored and controlled by a Hg/HgO (MMO) reference electrode.

The cell voltage, overall and anode activation overvoltages of AEMFC can be expressed using the equations below:

\[
E_{\text{cell}} = E_C - E_A = (E_{\text{theory, c}} - E_{\text{theory, A}}) - \left[ (|\eta_{\text{act, c}}| + \eta_{\text{act, A}}) + \eta_{\text{ohm}} + (\eta_{\text{tx, c}} + \eta_{\text{tx, A}}) \right] \tag{1}
\]

\[
\eta_{\text{act}} = \left( \frac{-2.303RT}{\alpha_nF} \right) \log(i) - \left( \frac{-2.303RT}{\alpha_nF} \right) \log(i_0) \tag{2, overall reaction}
\]

\[
\eta_{\text{act, A}} = \left( \frac{-2.303RT}{\alpha AnF} \right) \log(i) - \left( \frac{-2.303RT}{\alpha AnF} \right) \log(i_{A,0}) \tag{3, anode oxidation reaction}
\]

\(E_{\text{cell}}, E_C, E_A\) are the measured overall cell, cathode, and anode voltages. \(\eta_{\text{act}}\) is the activation overvoltage due to reaction kinetics loss. \(\eta_{\text{ohm}}\) is the ohmic overvoltage, due to combined ohmic resistance and charge transfer resistance. \(\eta_{\text{tx}}\) is the mass-transport overvoltage due to reactant transport limitation. \(\alpha\) is the electron transfer coefficient. Based on the anode activation polarization (\(\eta_{\text{act, A}}\)), important reaction kinetic data, such as the Tafel slope (b) and exchange current density (iA.0) can be obtained. b equals -2.303RT/\(\alpha AnF\). At a high working voltage (in the kinetic-control region), the measured kinetic current i gives mass activity. The specific activity is equal to mass activity / electrochemical active surface area (EASA), which can be obtained using in-situ cyclic voltammetry. The specific activity will be converted to 'absolute' activity: turnover frequency (TOF) for comparison with heterogeneous catalysis results. The \(\eta_{\text{tx}}\) can be obtained from \(i_{\text{lim}}\) collected in a regular
linear potential scan. An integrated frequency resistance analyzer in the fuel cell tester will be used to obtain an electrochemical impedance spectrum (EIS) from 1 m Hz to 10 kHz. The EIS can separate the ohmic resistance (mainly the ionic resistance of AEM) and charge transfer resistance (combined ionic and electric resistance in catalyst layer) using the Nyquist plot. This provides a sharp in situ technique to characterize the three-phase boundary of a MEA under real fuel cell working conditions for improving the overall AEMFC performance.

The reacted liquid mixture will be collected, diluted and filtrated for HPLC analysis. Selectivity of each product and conversion of biorenewable fuel under different operation conditions will be obtained. The carbon balance and electron balance (total electrons distributed to all detected products) will be calculated by taking account of fuel and product crossover (to cathode). To seek special voltage ranges to selectively produce valuable chemicals, different constant fuel cell operation voltages and different constant anode overpotentials (monitored and controlled through the MMO) will be held for different time periods to investigate the changes in selectivity of each product. Operation conditions, such as temperature, flow rate, ratio of base to fuel, ratio of catalyst to fuel, etc, will be thoroughly studied. The fuel will be supplied in both closed loop (with small 'dead volume') and open loop to study the reactor effects on the fuel conversion and product distribution.

Sufficient OH⁻ supply to the catalyst surface is a critical factor for enhancing reaction kinetics and regulating reaction pathways. 1-D carbon nanotubes / nanofibers, which could provide a continuous electric conduction and allow high anion exchange ionomer (AEI) content in catalyst layer, will have potential to use only AEI as the OH⁻ conductor. The cathode catalysts, e.g. Pt, Pd, Ag, FeCo-N/C (known for 4-electron oxygen
reduction in alkali) or Au (known for 2 electrons oxygen reduction in alkali), and oxidants, e.g. O₂ or H₂O₂ will change the cathode overpotential, thus influencing the overall electrooxidation. We will also study the cathode reaction to understand the roles of O₂ and OH⁻ in the overall selective electrooxidation in AEMFCs.

1.4 References


1.5 Detailed Projects Summary: The Target, Model Reaction, Strategy and Method of Detailed Projects in this Ph.D. Research are summarized in Table 1.2.

**Table 1.2** Target, model reaction, strategy and method of detailed projects in this Ph.D. research

<table>
<thead>
<tr>
<th>Target</th>
<th>Model Reaction</th>
<th>Strategy and Method</th>
</tr>
</thead>
</table>
| High performance fuel cell and products analysis baseline | Glycerol | 1. Synthesize highly active surfactant-free catalysts in water or ethanol solution with controlled morphology  
2. Demonstrate that pretreated crude glycerol can be directly used as fuel for high-performance anion exchange membrane (AEM) based active direct alcohol fuel cell  
3. Explain the benefits of such catalysts with density functional theory |
| C-N bond activation | Carbohydrazide | 1. Develop anode metal catalyst free and complete metal catalyst free direct carbohydrazide anion exchange membrane fuel cell (AEMFC) with carbon anode catalyst  
2. Calculate average electron number of electrons transferred per carbohydrazide molecule to evaluate the fuel efficiency. Confirm the C-N bond cleavage by product analysis |
### C-C bond protection

| Glycerol | 1. Optimize testing condition to on monometallic catalyst and lower down the anode potential and thus prevent the C-C bond from being cleaved  
2. Evaluate the desorbed reaction intermediates on different catalysts to explain the reaction pathway  
3. Design bimetallic catalyst according to their catalytic activity towards reaction intermediates to cogenerate electricity and tartronate from glycerol oxidation with maximum yield |

### C-H bond activation

| Aldehyde group | 1. Develop a descriptor with semi-empirical or density functional theory (DFT) method for catalysts evaluation for electrocatalytic aldehyde oxidation reaction  
2. Use this descriptor to screen catalysts in Lewis soft acids and compare the turnover frequencies of the best catalysts by half-cell experiments  
(This part has only unpublished results.) |
Table 1.2 continued

<table>
<thead>
<tr>
<th>C-C bond activation</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-polyol</td>
<td></td>
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</tbody>
</table>

3. Design bimetallic catalyst for alcohol oxidation with well-defined active sites for initial deprotonation and aldehyde intermediate oxidation, and demonstrate in single fuel cell

1. According to the activity of monometallic catalysts toward reaction intermediates, design bimetallic catalyst to cleave the C-C bond at low overpotential for highest bond scission rate in fuel cell anode potential window to maximize the fuel efficiency

2. Expand the scope of substrate to further verify the hypothesis
CHAPTER 2 HIGH PERFORMANCE FUEL CELL AND PRODUCTS ANALYSIS

BASELINE

2.1 Surface Dealloyed PtCo Nanoparticles Supported on Carbon Nanotube: Facile Synthesis and Promising Application for Anion Exchange Membrane Direct Crude Glycerol fuel cell

2.1.1 Graphical abstract

Figure 2.1 Graphical abstract of section 2.1.

This chapter is adapted from a published paper (Ji Qi, Le Xin, Zhiyong Zhang, Kai Sun, Haiying He, Fang Wang, David Chadderdon, Yang Qiu, Changhai Liang, Wenzhen Li, Surface dealloyed PtCo nanoparticles supported on carbon nanotube: facile synthesis and promising application for anion exchange membrane direct crude glycerol fuel cell, Green Chem., 15 (2013) 1133-1137). This research established a high performance fuel cell baseline with a high surface area catalyst, which was designed by creating surface roughness with ex-situ dealloy technique.
2.1.2 Abstract

Exploring crude glycerol as fuel for DAFC not only provides a promising solution to using excessive biodiesel byproduct, but also opens a new avenue towards development of low-cost alcohol fuel cells. In the present study, surface dealloyed PtCo nanoparticles supported on carbon nanotube (SD-PtCo/CNT) were prepared by ex situ method and used for crude glycerol oxidation for the first time. SD-PtCo/CNT anode catalyst based AEMFC with a 0.5 mgPt cm\(^{-2}\) achieved peak power densities of 268.5 mW cm\(^{-2}\) (crude glycerol/O\(_2\)) and 284.6 mW cm\(^{-2}\) (high purity glycerol/O\(_2\)) at 80 °C and ambient pressure, which are close to the published result of direct high purity glycerol SOFC operated at high temperature of 800 °C (327 mW cm\(^{-2}\)), and are higher than all other published performances of direct high purity glycerol MFC and AEMFC. This work successfully developed a high output power DAFC with biorenewable, environmentally-friendly fuel and dealloy technique prepared catalyst, which will substantially impact future catalyst design and fuel cell development.

2.1.3 Introduction

Due to the fast growth of global energy needs and quickly diminishing of fossil fuel resources, people are forced to seek reliable, high performance, cost-effective and environmentally-beneficial renewable energy sources.[1] Anion exchange membrane (AEM) based direct alcohol fuel cells (DAFCs) have recently attract enormous attention as a potential solution to alleviate the current energy issues.[2] In high pH media, the reaction kinetics of oxygen reduction reaction (ORR) at the cathode can be greatly improved due to facilitated
charge transfer, and therefore non-precious metal catalysts, such as Ag[3]. Fe/Co based catalyst[4, 5] can be employed. The mild alkaline electrolyte offers a friendly reaction environment to prevent catalyst from severe degradation. The permeability of alcohol is significantly reduced due to electroosmotic drag, and the operation voltage drop resulted from alcohol cross-over can be alleviated. However, the sluggish kinetics of anode alcohol oxidation (accordingly high precious metal loading), low alcohol fuel utilization, and high fuel cost remain the main technical obstacles hindering wide-spread applications of AEM-based DAFCs.

Crude glycerol has been mass-produced as a byproduct with currently blooming biodiesel manufacturing.[6] Due to the high cost of its purification, crude glycerol are just treated as waste, disposed by many bio-diesel plants.[7] Therefore, crude glycerol, including a 70-90 wt% pretreated one, is very cheap ($0.74-0.89 gal⁻¹) compared to refined alcohol (> $1.3 gal⁻¹, ESI† Table 2.S1). Here we suggest using crude glycerol as fuel of DAFC, which not only lowers fuel price but also achieves higher fuel efficiency than C₂⁺ mono-alcohol (such as ethanol, propanol and butanol). This is because crude glycerol can gives out more electrons than C₂⁺ mono-alcohol from partial oxidation without C-C bond cleavage, which is difficult at relatively low fuel cell operating temperature (e.g. ≤ 80 °C)[8-10]. As the final product is tartronate and mesoxalate, the theoretical Faradaic efficiency of glycerol oxidation is as high as 57.1% and 71.4%, making high energy density (24.0 MJ L⁻¹) of glycerol a more meaningful fuel.

Platinum (Pt) has high activity towards electro-oxidation of alcohol, and it is also the best identified monometallic electro-catalyst to break the C-C bond of C₂⁺ alcohols at relatively
low temperature.[11] Therefore, Pt stands out as one of the most desired catalyst to achieve high power density and fuel utilization efficiency. However, Pt is very expensive (>50 g⁻¹) due to its rare reserve in the earth crust, and is still more easily contaminated than other precious metals, e.g. Pd[12], although the intermediate poisoning can be alleviated to some extent due to weak bonding of chemisorbed intermediates in alkaline media[13]. These drawbacks limit its activity and reaction stability. Rational design of Pt-based catalysts with highly active and self-detoxicating active sites, and superior durability is of critical importance for developing direct alcohol fuel cell technologies.

Previous research efforts have been made on Pt-based binary and ternary surface dealloyed catalysts, Pt-M (M = Ni[14], Cr[14], Co[15], Cu[16], Fe[17],) for oxygen reduction reaction (ORR) with enhanced mass activity at the PEMFC cathode. However, the in situ volammetric dealloy methods are not practical in real large-scale syntheses,[18] and very little work has been carried out to study the electro-oxidation of alcohols over the promising dealloyed catalysts. Carbon nanotube (CNT) supported Pt catalysts with good dispersion, large electrochemically active surface area (ECSA) have exhibited high specific and mass activity,[19] and showed great potential to be used in DAFC fed with methanol[19] and ethanol[20].

In this work, surface dealloyed PtCo nanoparticles supported on carbon nanotube (SD-PtCo/CNT) was prepared via an ex situ method and used for glycerol oxidation for the first time. The SD-PtCo/CNT catalyst has a PtCo core and rough Pt-rich shell structure, which offers several advantages. First, the lattice strain of surface dealloyed nanoparticles and the interaction between surface platinum atoms and sub-layer Co atoms will lower the d band
center of the platinum, leading to weakened chemisorption of oxygenated species.[16, 21] The rate-determining step (RDS) of alcohol oxidation in alkaline media was accelerated due to the removal of adsorbed intermediates by adsorbed hydroxyl anions.[22] Thus, the Pt poisoning problem is alleviated by enhanced refreshment of active sites. Second, for a single particle with same size, dealloyed Pt nanoparticle has higher surface roughness and larger Pt surface area compared to conventional mono-metallic or multi-metallic nanoparticles, thus leading to higher electrochemical active surface area (ECSA). Third, multiwall carbon nanotube supports will form three dimensional network structures,[23] resulting in enhanced mass transfer of alcohol and OH\(^-\). An unprecedented performance of 268.5 mW cm\(^{-2}\) has been achieved by using the SD-PtCo/CNT anode catalyst with only 0.5 mg\(_{Pt}\) cm\(^{-2}\) in a membrane electrode assembly (MEA, with a commercial Fe-based cathode) for the direct crude glycerol (88 wt%) /O\(_2\) AEMFC operated at 80 °C and ambient pressure. Alcohol and OH\(^-\). An unprecedented performance of 268.5 mW cm\(^{-2}\) has been achieved by using the SD-PtCo/CNT anode catalyst with only 0.5 mg\(_{Pt}\) cm\(^{-2}\) in a membrane electrode assembly (MEA, with a commercial Fe-based cathode) for the direct crude glycerol (88 wt%) /O\(_2\) AEMFC operated at 80 °C and ambient pressure.

2.1.4 Experimental section

**Chemicals**

Sodium borohydride (99%) and high purity glycerol (99%) were purchased from Acros Organics. Carboxyl group functionalized multiwall carbon nanotube (CNT) was obtained from Cheaptubes Inc. Chloroplatinic acid hydrate (37%-40% Pt) and cobalt chloride hexahydrate
(98%) was bought from Sigma-Aldrich Co. Crude glycerol (88%, a byproduct from soy biodiesel manufacturing) was gained from Kingdom Bio Solutions Inc. All the chemicals were used as received without further purification.

**Synthesis of surface dealloyed PtCo supported on carbon nanotube**

Chloroplatinic acid hydrate (130.1 mg) and cobalt chloride hexahydrate (59.6 mg) were mixed together with carboxyl group functionalized multiwall carbon nanotube (180.3.0 mg) in 500 ml ethanol, followed by 30 minutes ultrasonic treatment so as to ensure that all of them are well-dispersed. After that, the mixture was kept in ice water for 5 minutes, which will prevent it from becoming too hot during the subsequent reduction process. Sodium borohydride (360 mg) was dissolved in ethanol (100 ml) and then blended with the above mixture to reduce and deposit the PtCo nanoparticles onto the surface of carbon nanotube. After filtrating and washing with 300ml deionized water and ethanol mixed solution (1:4 in volume), the PtCo/CNT was collected and dried in vacuum oven under 50℃ overnight. PtCo/CNT (100 mg) was then re-dispersed into 300 ml ethanol by 10 minutes ultrasonic treatment. 0.5 M hydrochloric acid (400 ml) in ethanol was added to the mixture to process the surface dealloy treatment. 15 minutes later, the SD-PtCo/CNT was collected by filtration and washing with another 200ml ethanol. Finally, SD- PtCo/CNT was collected and dried in vacuum oven under 50℃ overnight. Pt/CNT was synthesized via similar process as PtCo/CNT. All the catalysts in the experiment were controlled to have a Pt loading of 20%.
Structure and morphology characterization

The structure, composition and morphology of Pt/C, Pt/CNT, SD-PtCo/CNT catalysts were characterized by X-ray diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES), transmission electron microscopy (TEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). XRD patterns were collected by a Scintag XDS-2000 θ/θ diffractometer using Cu Kα radiation (λ = 1.5406 Å) with a filament current of 35 mA and a tube voltage of 45 kV. TEM was performed on JEOL 2010, operated at voltage of 200 kV. TEM analysis included HAADF-STEM with the spatial resolution of ~1.7 Å. The catalyst were dissolved in aqua regia solution (‘royal water’) over night before conducting ICP-AES test.

Half-cell test procedure

A conventional three-electrode, water jacket integrated glass cell for rotating electrodes (AFCELL3, Pine Instrument) with a glassy carbon working electrode (AFE3T050GC, Pine Instrument), a Hg/HgO reference electrode (MMO, CHI152, CH Instruments), and a Pt wire counter electrode (AFCTR1, Pine Instrument), was employed for cyclic voltammetry (CV) and linear scan voltammetry (LSV) experiments of the commercial Pt/C (Etek), as-prepared Pt/CNT and SD-PtCo/CNT catalysts at room temperature. Unless specified otherwise, all potentials in the present research were referred to MMO (1.0 M KOH, 0.098 V vs. SHE). Uniformly dispersed catalysts ink with a concentration of 1 mg/mL is acquired by ultrasonically treating a mixture of 2.0 mL iso-propanol and 2.0 mg catalysts in ice-water bath for 10 minutes. After polishing the glassy carbon electrode (GCE) with alumina micropolish
solution and grinding paper, 10 µl of the ink was dropwise added and evenly distributed over the surface of GCE. The electrolyte solution was under 99.999% high purity N2 protection during the whole experimental process. The scan rate is 50 mV s⁻¹ for cyclic voltammetry (CV) test, and 1 mV s⁻¹ for linear scan voltammetry (LSV). All half-cell test were completed under room temperature.

**Single-cell test procedure**

Fuel cell test system (850e Scribner-Associates) with self-made membrane electrode assembly (MEA), serpentine graphite flow field plate, and feedback temperature control loop composed of electric heating rods and thermocouple thermometer, was introduced to acquire polarization curve, power density curve and single cell inner resistance. MEA with an active area of 5cm² is composed of carbon cloth as anode catalyst substrate, anion exchange membrane (A901 Tokuyama), carbon paper as cathode backing layer. Anode catalyst substrate, obtained by spraying catalyst ink onto carbon cloth, had 0.5 mg/cm² metal loading of Pt/C, Pt/CNT, SD-PtCo/CNT catalysts. Before spraying, 15 mg/cm³ concentration catalyst ink, utilizing iso-propanol as solvent and 5% polytetrafluoroethylene (PTFE Teflon® Dupont) as binder (catalyst:PTFE=9:1 mass ratio), was ultra-sonicated in ice-water bath for 30 min so as to be uniformly distributed. Cathode is prepared by spraying mixture (catalyst:ionomer=7:3 mass ratio) of 3.5wt% non-noble metal loading commercial catalyst (4020 Acta) and ionomer (AS-4 Tokuyama) onto anion exchange membrane (A901 Tokuyama), subsequently followed by covering carbon paper as cathode backing layer.
Glycerol conversion analysis

High-performance liquid chromatography (HPLC, Agilent 1100) with a refractive index detector (RID), a variable wavelength detector (VWD) and an OA-1000 column (Alltech) was employed to quantify the conversion of glycerol in active direct glycerol fuel cell operated at different potentials. The temperature of column was 60 °C. 5 mM H$_2$SO$_4$ was used as mobile phase with a flow rate of 0.3 mL min$^{-1}$. The sample volume was controlled to be 20 $\mu$L.

Particle size and lattice constant calculation based on XRD testing

A representative set of XRD patterns for Pt/C (Etek), Pt/CNT and SD-PtCo/CNT catalysts are shown in Fig 2(E) in the main article, which indicates that the metal particles have the face-centered cubic (FCC) structure. Typical for nanosized materials, the diffraction peaks are fairly board. The mean crystallite size of Pt/C (Etek), PtCo/CNT and SD-PtCo/CNT catalysts are calculated using the (220) peak based on Debye-Scherrer formula, while lattice constants for Pt/C (Etek), PtCo/CNT and SD-PtCo/CNT catalysts are calculated using the (220) peak based on the combination of Bragg's law and the relationships between lattice constant and crystal lattice spacing:

$$L = \frac{0.9\lambda_{K\alpha}}{B\theta \cos \theta_{\text{max}}}$$
$$a_{\text{fcc}} = \frac{\sqrt{2}\lambda_{K\alpha}}{\sin \theta_{\text{max}}}$$

Where L is the mean crystallite size, $\lambda_{K\alpha}$ is the wavelength of the X-ray (1.5406 Å), B is the full width at half-maximum (FWHM) of the peak (rad), $\theta_{\text{max}}$ is the Bragg angle (rad) of
(220) peak position, and $a_{fcc}$ is the lattice constant for face-centered cubic (FCC) structure. According to the above-mentioned equation, the mean crystallite size of the metal particles on the Pt/C (Etek), Pt/CNT, PtCo/CNT and SD-PtCo/CNT catalyst is 1.9 nm, 2.9 nm, 2.1 nm, 2.2 nm while the lattice constant of them is 3.944 Å, 3.918 Å, 3.834 Å, 3.808 Å, respectively.

**Catalyst loading and atomic ratio based on ICP-AES**

The Pt loading of PtCo/CNT and SD-PtCo/CNT is 19.3% and 19.1% while the Pt:Co atomic ratio of them is 53:47 and 69:31, respectively, indicating that the precursor has been fully reduced and only the Co particle on the surface of the catalyst had been removed by dealloy treatment.

**2.1.5 Results and discussion**

![Diagram showing synthesis of surface dealloyed PtCo supported on CNT (SD-PtCo/CNT) catalyst.](image)

**Figure 2.2** Schematic illustration of synthesis of surface dealloyed PtCo supported on CNT (SD-PtCo/CNT) catalyst.
Figure 2.1 illustrates the schematic synthesis steps of SD-PtCo/CNT. The surface of CNT is grafted with carboxyl groups for anchoring metal particles. Bimetallic PtCo supported on CNT (PtCo/CNT) was prepared by simultaneously reducing two metal precursors with strong reducing agent NaBH₄ in an ethanol solvent containing well-dispersed CNT. Co atoms were subsequently removed from the surface of PtCo/CNT using diluted HCl. SD-PtCo/CNT with 20 wt% Pt loading was finally obtained with randomly distributed Pt and Co atoms inside the metal nanoparticle (See ESI† for detailed synthesis process).
Figure 2.3 TEM images and particle size histograms of (A) PtCo/CNT, (B) SD-PtCo/CNT; HAADF-STEM images of a single particle of (C) PtCo/CNT, (D) SD-PtCo/CNT; and (E) XRD patterns of Pt/C, Pt/CNT, PtCo/CNT and SD-PtCo/CNT (20 wt% Pt loading)

Figure 2.2 shows the transmission electron microscopy (TEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of
PtCo particles supported on CNT before and after surface dealloying and the XRD patterns of Pt/C, Pt/CNT, PtCo/CNT and SD-PtCo/CNT. Fig 2(A),(B) indicate that the bimetallic PtCo nanoparticles are well dispersed on CNT with uniform particle size distribution. The average particle size measured from randomly counting 100 particles is 2.2 nm and 2.3 nm for PtCo/CNT and SD-PtCo/CNT respectively, which is consistent with the X-ray diffraction (XRD) results calculated using the (220) diffraction peak (See ESI† for calculation details). As marked in Figure 2.2(C), the interplanar distance of PtCo/CNT is 0.135 nm and 0.189 nm for facet (220) and facet (200), which is 0.004 nm and 0.008 nm smaller than that of Pt/C, revealing the existence of lattice strain. This is further confirmed by the peak shift of PtCo/CNT compared with Pt/C and Pt/CNT (Figure 2.2E), which also demonstrates that PtCo is very well alloyed. The characterization results suggest that the presented dealloy technique will not only generate particles with surface roughness (Figure 2.2(D)), but also maintain the lattice-strained Pt skeleton structure, since no peak shift is observed for PtCo/CNT and SD-PtCo/CNT (Figure 2.2(E)).
Figure 2.3 shows the polarization and power density curves of single AEMFC with SD-PtCo/CNT anode catalyst at different operating temperatures. Higher temperature improves the glycerol oxidation kinetics, and thus leads to a higher fuel cell output power density. The open circuit voltage (OCV) of AEMFC operating at 25 °C, 40 °C, 60 °C and 80 °C is 0.74 V, 0.79 V, 0.80 V and 0.81 V, while the peak power density (PPD) is 35.5 mW cm⁻², 52.5 mW cm⁻², 91.5 mW cm⁻² and 141.4 mW cm⁻² respectively.

Figure 2.4 displays polarization and power density curves of a single cell with Pt/C, Pt/CNT, or SD-PtCo/CNT anode catalyst under optimized conditions (See ESI† Fig S1-S6 for single cell performance under different operating conditions). The OCV of the direct crude glycerol/O₂ AEMFC with SD-PtCo/CNT as anode catalyst is 0.86 V, which is 0.02 V higher than that with Pt/CNT, 0.07 V higher than that with Pt/C. While the PPD of direct crude glycerol/O₂ AEMFC with SD-PtCo/CNT as anode catalyst is 268.5 mW cm⁻², which is 17.6%
higher than that with Pt/CNT, and 37.1% higher than that with Pt/C. The mass activity based on single cell at 80 °C is 0.537 W mg\text{precious metal per MEA}^{-1}, which is among the highest published results for direct alcohol/O₂ low temperature fuel cell as far as we know. Moreover, the single cell performance of direct crude glycerol/air AEMFC is about two thirds of that of direct crude glycerol/O₂ AEMFC. It is also interesting to observe that crude glycerol fuel only result in 5.6% AEMFC performance drop compared to high-purity glycerol fuel (268.5 mW cm\(^{-2}\) vs 284.5 mW cm\(^{-2}\) ESI† Fig S7).

![Figure 2.5](image)

**Figure 2.5** Polarization and power density curves of direct crude glycerol/O₂ (or air) AEMFC with different anode catalysts (SD-PtCo/CNT, Pt/CNT and Pt/C (Etek), 0.5 mg\text{Pt cm}^{-2}) at optimized operating conditions. AEM: Tokuyama A901; cathode catalyst: Fe-Cu-N₄/C (Acta 4020), 3.0 mg\text{catalyst cm}^{-2}; anode fuel: 6.0 M KOH + 3.0 M crude glycerol (88 wt%), 4.0 ml min\(^{-1}\); cathode fuel: 200 sccm O₂ or 2000 sccm regular air, ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/80/80 °C.

Electrocatalytic oxidation of high-purity glycerol over the three catalysts in half cell was conducted to clarify their intrinsic activity towards glycerol oxidation. The sequence of mass activity, revealed by the onset potential and peak mass current density in the forward scan, is Pt/C(Etek) < Pt/CNT < SD-PtCo/CNT (ESI† Fig.S9), which is consistent with single
AEMFC test results. For Pt/CNT, its large particle size is compensated by the three dimensional network catalyst layer[23], leading to higher electrochemically active area (ECSA, ESI† Fig.S8) and specific activity (ECSA, ESI† Fig.S10), so that its mass activity is higher than Pt/C (ESI† Fig.S9, S10). For SD-PtCo/CNT, its ECSA further is enlarged (ESI† Fig.S8) due to smaller particle size and surface roughness, while its specific activity is enhanced by d-band center shift as a result of lattice strain and optimized electronic properties tuned by the sub-layer transitional atoms, so that its mass activity is much higher than Pt/CNT and Pt/C (ESI† Fig.S9,S10). The pseudo steady state mass activity after 20000 s chronoamperometry is 1.5 and 2.4 times that of Pt/CNT and Pt/C, confirming that the long-term activity towards glycerol oxidation has been improved by employing SD-PtCo/CNT (ESI† Fig.S11). The high intrinsic activity of SD-PtCo/CNT towards glycerol oxidation also provides high fuel utilization ratio in single AEMFC. Compared with Pt/C, SD-PtCo/CNT improves both fuel conversion (by 42.6%~59.2%) and fuel efficiency (by 14.3%~30.8%) at different operating cell voltages (ESI† Table 2.S2).
Figure 2.6 State-of-art glycerol fuel cell performances (See ESI† Table 2.S3 for comparison of experimental details). Peak power density versus operating temperature is exhibited for the major glycerol-fed fuel cell systems including microbial fuel cell (MFC)[24-28], anion exchange membrane fuel cell (AEMFC)[9, 10, 20, 29-32] and solid oxide fuel cell (SOFC)[33-35].

Figure 2.5 summarizes the state-of-art direct glycerol fuel cell performance based on the peak power density and operating temperature. Working at higher temperature, direct high-purity glycerol SOFCs have highest peak power density of 225 mW cm\(^{-2}\) (580 °C) and 327 mW cm\(^{-2}\) (800 °C). This is just slightly higher than the AEMFC performance reported in this work, which is 268.5 mW cm\(^{-2}\) (crude glycerol/O\(_2\)) and 284.6 mW cm\(^{-2}\) (high purity glycerol/O\(_2\)). It has been founded that OH\(^-\) facilitates alcohol oxidation in heterogeneous catalysis.[36] In this work, we demonstrated facile glycerol oxidation kinetics over dealloyed catalyst in high pH can generate very high electrical power in AEMFC. At 25 °C, 40 °C, 60 °C and 80 °C, the crude glycerol based AEMFC has 97.2 %, 64.1 %, 69.4 % and 78.0 % higher peak power density than the maximum published results of high purity glycerol based AEMFC, respectively. In
comparison, MFCs work under ambient temperature and pressure, but they only generate a peak power density of \(< 2 \text{ mW cm}^{-2}\), thus limiting its application to environmental remediation rather than practical energy technologies. SOFCs can generate higher electrical power, but they work at high temperature (i.e. \(> 580^\circ\text{C}\)) with material compatibility issues, thus limiting them to stationary applications.

2.1.6 Conclusions

We have firstly demonstrated that pretreated crude glycerol can be directly used as fuel for high performance AEM based active DAFC, which has the potential to substantially impact the development of DAFC technology. CNT supported surface dealloyed catalyst was employed as AEM based direct crude glycerol fuel cell anode catalyst, with which an unprecedented single cell performance (268.5 mW cm\(^{-2}\)) and catalytic mass activity (537 mW mg\(_{\text{precious metal per MEA}^{-1}}\)) is achieved under \(80^\circ\text{C}\) and ambient pressure. This performance was found to be comparable with that of SOFC operated under very high temperature (580-800 \(^\circ\text{C}\)), filling up the blank of low temperature high performance direct glycerol fuel cell.

2.1.7 Supporting information

**Comparison of different fuel from price and performance aspects**

The average price of crude glycerol is only $0.82 gal\(^{-1}\), which is 81.4\%, 38.8\%, 74.0\% lower than that of refined glycerol, methanol and ethanol, respectively. However, the performance of direct crude glycerol AEMFC is comparable to (only 5.65\% lower than) that of direct high purity glycerol AEMFC.
Table 2.S1 Comparison of fuel price and published results of highest performances of different fuel cells

<table>
<thead>
<tr>
<th>Fuel Source</th>
<th>Price in North America</th>
<th>Highest performance of AEMFC (low T &lt;100°C)</th>
<th>Highest performance of PEMFC (low T &lt;100°C)</th>
<th>Highest performance of SOFC (high T &gt;200°C)</th>
</tr>
</thead>
</table>
| Crude Glycerol  
(a minimum 85% glycerol, with low salts and MONG (many organics not glycerine)) | 7–10 cents lb⁻¹  
0.74-0.89 dollars gal⁻¹ | Results of this paper  
268.5 mW cm⁻²  
(0.5 mgPt cm⁻², 80 °C, O₂)  
200 mW cm⁻²  
(0.5 mgPt cm⁻², 80 °C, air) | Not available | Not available |
| Refined Glycerol  
4.00–4.84 dollars gal⁻¹ | 124.5 mW cm⁻²  
(1 mgPt cm⁻², 80°C, O₂) [10]  
Results of this paper  
284.6 mW cm⁻²  
(0.5 mgPt cm⁻², 80°C, O₂) | Not available | 327 mW cm⁻²  
(800°C) [34]  
215 mW cm⁻²  
(580°C) [35] |
| Methanol  
1.34 dollars gal⁻¹ | 168 mW cm⁻²  
(3.0 mgPtRu cm⁻², 90°C, O₂) [37] | 246 mW cm⁻²  
(90°C) [38] | 1600 mW cm⁻²  
(750°C) [39] |
| Ethanol  
3.15 dollars gal⁻¹ | 185 mW cm⁻²  
(1.2 mgPdAu cm⁻², 60°C using O₂) [40]  
240 mW cm⁻²  
(1 mgPt cm⁻², 60°C, using H₂O₂) [41] | 79.5 mW cm⁻²  
(90°C) [42] | 800 mW cm⁻²  
(800°C) [43]  
160 mW cm⁻²  
(580°C) [43] |
Direct crude glycerol fuel cell operated under different conditions

Figure 2.S1 Polarization and power density curves of direct crude glycerol/O₂ AEMFC with SD-PtCo/CNT as anode catalyst using different concentrations of crude glycerol. Anode catalyst (0.5 mg Pt cm⁻²): SD-PtCo/CNT (Self-prepared); anion exchange membrane: Tokuyama A901; cathode catalyst (3.0 mg catalyst cm⁻²): Fe-Cu-Nₓ/C (Acta 4020); anode fuel: 1.0 M KOH, 1.0 ml min⁻¹; cathode fuel: 100 sccm O₂, ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/60/60 °C.

Figure 2.S1 presents the crude glycerol concentration effects on polarization and power density curves of direct crude glycerol/O₂ AEMFC with SD-PtCo/CNT as anode catalyst. When crude glycerol concentration is above 1 M, cell voltage loss increases with crude glycerol concentration in all the current region. The first reason can be traced back to the increment of
single cell internal resistance, as presented in Figure 2.S2. In view of crude glycerol’s high viscosity, increment of its concentration will remarkably increase the viscosity of fuel solution, which will lower the mobility of anion and cation. The conductivity of the electrolyte is thus reduced, so that the single cell internal resistance increases. The second reason is linked to the depression of glycerol oxidation kinetics, as indicated by the OCV drop along with glycerol concentration accretion manifested in Figure 2.S2. On one hand, the hydroxyl anion’s mass transfer issue, emerged as crude glycerol concentration increases, will result in its concentration drop inside the anode catalyst layer. On the other hand, the amount of adsorbed hydroxyl anion on the catalyst active sites will decline when glycerol concentration is higher due to the competitive adsorption between hydroxyl anion and glycerol. To sum up, when the crude glycerol concentration increases from 1.0 M to higher value, single cell performance will decrease in all current region.

![Figure 2.S2](image)

**Figure 2.S2** The effect of crude glycerol concentration on open circuit voltage and internal resistance
When crude glycerol concentration changes from 0.5 M to 1.0 M, cell voltage is slightly increased in the low current region and is markedly increased in high current region. In the low current region, the oxidation rate of glycerol is relatively slow, wherefore 0.5 M and 1.0 M crude glycerol are all adequate to maintain an appropriate concentration in the anode catalyst layer corresponding to 1.0 M KOH. However, in the high current region, faster oxidation rate of glycerol will let the glycerol become the limiting reagent. Meanwhile under relatively low crude glycerol concentration, crude glycerol increasing has limited effect on single cell IR (Figure 2.S2) and hydroxyl anion mobility, making glycerol mass transfer the bottle neck of GOR kinetics. Therefore 1.0 M crude glycerol promotes the single cell performance compared to 0.5 M crude glycerol mainly by alleviating glycerol mass transfer issue in high current density region.
Figure 2.S3 Polarization and power density curves of direct crude glycerol/O₂ AEMFC with SD-PtCo/CNT as anode catalyst using different KOH concentration. Anode catalyst (0.5 mgPt cm⁻²): SD-PtCo/CNT (Self-prepared); anion exchange membrane: Tokuyama A901; cathode catalyst (3.0 mg catalyst cm⁻²): Fe-Cu-N₄/C (Acta 4020); anode fuel: 1.0 M crude glycerol, 1.0 ml min⁻¹; cathode fuel: 100 sccm oxygen, ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/60/60 °C.

As shown in Figure 2.S3, the cell voltage increases with KOH concentration in the low current density region (<100 mA cm⁻²). Higher KOH concentration facilitates the dehydrogenation of glycerol’s \( H_a \), leading to a higher concentration of alkoxide ion which is an
active precursor to aldehyde formation, so that the subsequent elimination of $H_\beta$ in anode catalyst layer is enhanced\cite{44}.

\[ H_\beta R - OH_a \rightleftharpoons H_\beta R - O^- + H_a^+ \]

\[ H_\beta R - O^- \rightarrow R = 0 + H_\beta^+ + 2e^- \]

Moreover, higher KOH can neutralize the organic acid generated during the glycerol oxidation process. The local concentration of KOH is thus maintained to a level adequate for oxidizing glycerol continuously. Therefore, higher KOH concentration is favorable toward glycerol oxidation kinetics. It is worth mentioning that the amount of glycerol in anode catalyst layer is high enough to prevent the system from being limited by mass transfer issue in the low current density region. Based on the above discussion, it can be concluded that higher KOH concentration will boost the single cell performance monotonically in the low current density region.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_2.S4}
\caption{The effect of KOH concentration on the open circuit voltage and internal resistance}
\end{figure}
In the high current density region (>250 mA cm\(^{-2}\)), the cell voltage increases as KOH concentration changes from 0 M to 6.0 M and then decreases when the KOH concentration further increases from 6.0 M to 10.0 M. This phenomena can be explained by the simultaneous effect of some contrary trends. Higher concentrations of KOH will promote the glycerol oxidation kinetics, as indicated by the rising trend of OCV shown in Figure 2.S4. A thicker membrane (Tokuyama A201, 28 \(\mu m\)) was adopted in the experiment of AEM based direct ethanol and ethylene glycol fuel cell by Zhao and co-workers\([45, 46]\). It’s found that the internal resistance (IR) is mainly affected by the conduct resistance of hydroxyl anion from cathode side to anode side in the AEM. Hence the single cell IR increases monotonically with rising KOH concentration. However, AEM (Tokuyama A901, 10 \(\mu m\)) adopted in this work is relatively thinner, whereupon the single cell IR is principally dependent on the electric conductivity of the electrolyte. At 60\(^\circ\)C, the electric conductivity of the KOH water solution will first increase and then decrease when KOH varying from 0 M to 12.0 M, reaching its maximum value at 6.0-7.0 M\([47]\). Thereupon, the single cell IR increases as KOH concentration changes from 0 M to 6.0 M and then decreases when KOH concentration further increases from 6.0 M to 10.0 M. Moreover, the adsorption of hydroxyl anion and glycerol is competitive. Too much hydroxyl anion will prevent glycerol from being adequately adsorbed onto the active sites of anode catalyst layer, for the reason that in the high current density region the corresponding consumption rate of glycerol is high. When the KOH concentration rises from 0 M to 6.0 M, the positive effect of internal resistance decline and glycerol oxidation kinetics enhancement surpass the negative effect of competitive adsorption caused mass transfer issue. When the KOH concentration further increases from 6.0 M to 10.0 M, the
negative effect of internal resistance upswing and mass transfer issue will become dominant other than the positive effect of glycerol oxidation kinetics enhancement. All in all, the uptrend of KOH concentration will simultaneously promote and depress the performance for AEM based direct crude glycerol fuel cell.

**Figure 2.S5** Polarization and power density curves of direct crude glycerol/O₂ AEMFC with SD-PtCo/CNT as anode catalyst using different cathode oxygen flow rate. Anode catalyst (0.5 mgPt cm⁻²): SD-PtCo/CNT (Self-prepared); anion exchange membrane: Tokuyama A901; cathode catalyst (3.0 mg Catalyst cm⁻²): Fe-Cu-N₄/C (Acta 4020); anode fuel: 2.0 M KOH + 1.0 M crude glycerol, 1.0 ml/min; cathode fuel pressure: ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/60/60 °C.
As demonstrated in Figure 2.5, oxygen flow rate has little effect on cell voltage in low current density region. Although not remarkable, it can still be seen that the cell voltage in the mass controlled region will first increase and then decrease with the accretion of oxygen flow rate, indicating the existence of a trade-off between positive effects and negative effects. Higher oxygen flow rate will facilitate its mass transfer, leading to enhanced oxygen reduction reaction (ORR) kinetics so that the single cell performance increases with oxygen flow rate ranging from 50 sccm to 200 sccm. However, the ORR reaction is simultaneously affected by oxygen and water mass transfer due to consumption of water at AEMFC cathode side:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]

If oxygen flow rate is further increased, water on the cathode side will be physically swept out from the cathode catalyst layer. The consequent membrane dryness will deteriorate the water mass transfer for ORR. When the oxygen flow rate increases from 200 sccm to 2000 sccm, single cell performance will decline in the mass transfer controlled region for the reason that the negative effect of water mass transfer outstrips the positive effect of oxygen mass transfer for ORR.
Figure 2.S6 Polarization and power density curves of direct crude glycerol/O$_2$ AEMFC with SD-PtCo/CNT as anode catalyst using different anode fuel flow rate. Anode catalyst (0.5 mg$\text{Pt}$ cm$^{-2}$): SD-PtCo/CNT (Self-prepared); anion exchange membrane: Tokuyama A901; cathode catalyst (3.0 mg$\text{catalyst}$ cm$^{-2}$): Fe-Cu-N$_4$/C (Acta 4020); anode fuel concentration: 2.0 M KOH + 1.0 M crude glycerol; cathode fuel: 100 sccm O$_2$, ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/60/60 °C.

Data in Figure 2.S6 shows no distinct influence of anode fuel flow rate on cell voltage, especially in the low current region. In the high current density region, higher glycerol and KOH consumption rate will be compensated by better mass transfer of glycerol and hydroxyl anion in the anode catalyst layer as a result of higher fuel flow rate, which can be regarded as the reason for the slight increase of single cell performance.
Figure 2.S7 Polarization and power density curves of direct crude glycerol/O_2 AEMFC with SD-PtCo/CNT as anode catalyst using high purity and crude glycerol. Anode catalyst (0.5 mgPt cm\(^{-2}\)): SD-PtCo/CNT (Self-prepared); anion exchange membrane: Tokuyama A901; cathode catalyst (3.0 mg\(_{\text{catalyst}}\) cm\(^{-2}\)): Fe-Cu-N\(_{4}\)/C (Acta 4020); electrolyte concentration: anode fuel concentration: 6.0 M KOH+3.0 M high purity & crude glycerol; anode fuel flow rate: 4.0 ml min\(^{-1}\); cathode fuel flow rate: 200 sccm O\(_2\), ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/80/80 °C.

The cell voltage of high purity glycerol based AEMFC is slightly higher than the counterpart of crude glycerol based AEMFC, which is attributed to some impurities in the crude glycerol. The peak power density of high purity glycerol based AEMFC (284.6 mW cm\(^{-2}\)) is
only 16.1 mW cm\(^{-2}\) higher than that of crude glycerol based AEMFC (268.5 mW cm\(^{-2}\)), revealing that the impurities in crude glycerol does not have remarkable effect on glycerol’s adsorption on the anode catalyst active sites.

**Comparison of glycerol oxidation on SD-PtCo/CNT, Pt/CNT, Pt/C in three-electrode one-compartment cell**

![Comparison of electrolytically active area (ECSA) calculated from platinum reduction peak (For poly polycrystalline Pt electrode, its oxide reduction process has a pseudo-capacity of 0.440 mC cm\(^{-2}\))\(^{[48]}\) obtained on Pt/C, Pt/CNT and SD-PtCo/CNT in 1.0 M KOH at 50 mV s\(^{-1}\) under room temperature. The scan range is from -0.9 V to 0.4 V vs. MMO.](image)

Although the particle size of Pt/CNT (2.9 nm) is larger than that of Pt/C (1.8 nm) according to XRD results, its ECSA is still larger than that of Pt/C owing to the higher exposure
level of Pt particles offered by the three dimensional network catalyst layer.\cite{23} The ECSA of SD-PtCo/CNT is higher than that of Pt/CNT due to surface roughness and smaller particle size of Pt particles.

**Figure 2.S9** Cyclic voltamgrams of Pt/C, Pt/CNT and SD-PtCo/CNT for glycerol oxidation in N$_2$ purged 2.0 M KOH + 1.0 M glycerol at 50 mV s$^{-1}$ at room temperature.

Although the Pt/C catalyst has smaller particle size, the network structure of Pt/CNT catalyst layer in three dimensional space\cite{23} offers more active sites, better glycerol and hydroxyl anion mass transfer and electron transfer than Pt/C does, especially when catalyst supports are packed up with each other. Accordingly, the onset potential of Pt/CNT for glycerol oxidation CV curve is 50 mV more negative than that of Pt/C while the peak current mass
activity of Pt/CNT is 1.20 mA $\mu$g$^{-1}$ higher than that of Pt/C. As discussed in the article, the dealloy technique facilitates the rate determining step (RDS) of glycerol oxidation and enlarge the catalyst ECSA, thus boosting the glycerol oxidation reaction rate. Consequently, so that the onset potential of SD-PtCo/CNT for glycerol oxidation CV curve is more negative (100 mV) than that of Pt/CNT while the peak current mass activity of SD-PtCo/CNT is higher (2.22 mA $\mu$g$^{-1}$) than that of Pt/CNT.

**Figure 2.S10** Linear scan voltammograms of of Pt/C, Pt/CNT and SD-PtCo/CNT for glycerol oxidation in N$_2$ purged 2.0 M KOH + 1.0 M glycerol at 1 mV s$^{-1}$ at room temperature.

The onset potential, peak current density, mass activity at -0.5 V and specific activity at -0.5 V shown in Figure 2.S10 indicate that the catalyst activity toward glycerol oxidation is SD-PtCo/CNT > Pt/CNT > Pt/C, which is consistent with results of ECSA test, fast CV scan
and single cell performance. For Pt/CNT, the combine effect of its larger ECSA and higher specific activity as a result of enhanced mass transfer of glycerol and OH\(^-\) leads to its higher mass activity than Pt/C. For SD-PtCo/CNT, its ECSA is further enlarged while its specific activity is improved by d-band center shift owing to compressed lattice and optimized electronic properties tuned by the sub-layer transitional metal atoms, resulting in much higher mass activity than Pt/CNT and Pt/C.

**Figure 2.S11** Chronoamperometric profiles of of Pt/C, Pt/CNT and SD-PtCo/CNT for glycerol oxidation in 2.0 M KOH and 1.0 M glycerol at 1 mV s\(^{-1}\) under room temperature

The chronoamperometric profiles in Figure 2.S11 obtained at the electrode applied voltage of -0.5 V (vs. MMO) also compare the prepared catalysts activity towards glycerol
oxidation. The target potential was held for 20000s to obtain a pseudosteady state current density profile. At 20000s, the pseudosteady state mass activity decreases in the order SD-PtCo/CNT > Pt/CNT > Pt/C, indicating that the long-term activity towards glycerol oxidation has been improved by employing SD-PtCo/CNT.

**Fuel conversion and efficiency analysis**

\[
Fuel \ conversion = \frac{C_0 - C_f}{C_0}
\]

\(C_0\) is the concentration of glycerol supplied to the single cell chamber, while \(C_f\), quantified by HPLC, is the concentration of glycerol coming out of the single cell chamber.

\[
Fuel \ efficiency = \frac{Q_{\text{actual}}}{Q_{\text{total}}} = \frac{\int_{t_0}^{t_f} I(t) dt}{nMF}
\]

\(Q_{\text{actual}}\) is actual charge passing through external circuit, while \(Q_{\text{total}}\) is the theoretical charge released by supplied reagent assuming that the selectivity to target product is 100\%. \(t_0\) and \(t_f\) is the reaction start and stop time, respectively. \(I\) is the current of external circuit recorded by fuel cell test stand. \(n\) refers to the electrons released by one reagent molecule when it is converted to target product. When the target product of glycerol oxidation is carbon dioxide, \(n\) equals 14. \(x\) is the conversion of supplied reagent. \(M\) is the total mole amount of reagent supplied between \(t_0\) and \(t_f\). \(F\) is Faraday constant (96485.33 C mol\(^{-1}\)).
Figure 2.S12 Transient cell current of the direct glycerol fuel cell with Pt/C and SD-PtCo/CNT as anode catalyst at different cell voltages. AEM: Tokuyama A901; cathode catalyst: Fe-Cu-N4/C (Acta 4020), 3.0 mg catalyst cm⁻²; anode fuel: 6.0 M KOH + 3.0 M crude glycerol (88 wt%), 1.0 ml min⁻¹; cathode fuel: 100 sccm O₂, ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/60/60 °C.
Table 2.S2 Fuel conversion and efficiency comparison for Pt/C and SD-PtCo/CNT

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cell Voltage</th>
<th>Fuel Conversion</th>
<th>Fuel Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>0.5</td>
<td>7.94 %</td>
<td>2.60 %</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.3</td>
<td>13.87 %</td>
<td>6.14 %</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.1</td>
<td>19.14 %</td>
<td>8.39 %</td>
</tr>
<tr>
<td>SD-PtCo/CNT</td>
<td>0.5</td>
<td>12.64 %</td>
<td>3.40 %</td>
</tr>
<tr>
<td>SD-PtCo/CNT</td>
<td>0.3</td>
<td>20.82 %</td>
<td>7.02 %</td>
</tr>
<tr>
<td>SD-PtCo/CNT</td>
<td>0.1</td>
<td>27.30 %</td>
<td>10.53 %</td>
</tr>
</tbody>
</table>

Products is collected when current is steady (from 3 min to 8 min) so as to conduct HPLC analysis. As shown in Figure 2.S12, the single cell with SD-PtCo/CNT as anode catalyst generates higher current than the one with Pt/C does at every operating cell voltage, which is consistent with the results of fuel conversion and fuel efficiency as displayed in Table 2.S3, indicating that SD-PtCo/CNT can be used as efficient anode catalyst with enhanced fuel utilization for active AEM based direct glycerol fuel cell.
State-of-the-art of direct glycerol fuel cells

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>Fuel composition</th>
<th>Anode catalyst</th>
<th>Cathode catalyst</th>
<th>Electrolyte</th>
<th>Temperature °C</th>
<th>*PPD (mW cm⁻²)</th>
<th>Mass activity (**)Unit</th>
<th>Ref</th>
</tr>
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<tr>
<td>SOFC</td>
<td>Glycerol/water(1:3)</td>
<td>Ni</td>
<td>LSM</td>
<td>YSZ</td>
<td>650, 750, 800</td>
<td>125, 225, 265</td>
<td>[33]</td>
<td></td>
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<tr>
<td>SOFC</td>
<td>High purity glycerol</td>
<td>Ni on LSFCO</td>
<td>CGO</td>
<td>LSFCO-CGO</td>
<td>800</td>
<td>327</td>
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<td>[34, 49, 50]</td>
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<tr>
<td>SOFC</td>
<td>Glycerol/water(50 wt%)</td>
<td>LNCO-NSDC</td>
<td>LNCO-NSDC</td>
<td>NSDC</td>
<td>580</td>
<td>215</td>
<td></td>
<td>[35]</td>
</tr>
<tr>
<td>AEMFC</td>
<td>6.0 M KOH 3.0 M Crude &amp; High purity glycerol</td>
<td>SD-PtCo/CNT 0.5 mgPt cm⁻²</td>
<td>Fe-Cu-Ni/C</td>
<td>Tokuyama A901</td>
<td>80</td>
<td>268.5 (Crude glycerol) 284.6 (High purity glycerol)</td>
<td>537 569.2 (This work)</td>
<td></td>
</tr>
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<td>AEMFC</td>
<td>2.0 M KOH 1.0 M Crude glycerol</td>
<td>SD-PtCo/CNT 0.5 mgPt cm⁻²</td>
<td>Fe-Cu-Ni/C</td>
<td>Tokuyama A901</td>
<td>25, 40, 60, 80</td>
<td>35.5, 52.5, 91.5, 141.4</td>
<td>71 105 183 282.8 (This work)</td>
<td></td>
</tr>
<tr>
<td>AEMFC</td>
<td>1.0 M Glycerol 2.0 M KOH</td>
<td>Pt/C 1.0 mgPt cm⁻²</td>
<td>Fe-Cu-Ni/C</td>
<td>Tokuyama A201</td>
<td>50, 80</td>
<td>58.6, 124.5</td>
<td>58.6 124.5 (This work)</td>
<td>[10]</td>
</tr>
<tr>
<td>AEMFC</td>
<td>Glycerol (5%wt) 2.0 M KOH</td>
<td>Pd-(Ni-Zn)/C 1.0 mgPd cm⁻²</td>
<td>Fe-Co/C</td>
<td>Tokuyama A-006</td>
<td>22, 80</td>
<td>24, 100</td>
<td>24 100 (This work)</td>
<td>[31]</td>
</tr>
<tr>
<td>AEMFC</td>
<td>1.0 M Glycerol 2.0 M KOH</td>
<td>Au/C 1.0 mgAu cm⁻²</td>
<td>Fe-Cu-Ni/C</td>
<td>Tokuyama A201</td>
<td>50, 70, 80</td>
<td>17.5, 26.3, 37.1, 57.9</td>
<td>17.5 26.3 37.1 57.9 (This work)</td>
<td>[9]</td>
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<tr>
<td>AEMFC</td>
<td>Glycerol (5%wt) 2.0 M KOH</td>
<td>Pd/CNT 1.0 mgPd cm⁻²</td>
<td>Fe-Co/C</td>
<td>Tokuyama A-006</td>
<td>25, 40, 60, 80</td>
<td>18, 32, 54, 79</td>
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<td>Glycerol (25%wt) 3.0 M KOH</td>
<td>Pt-Ru/C 0.5 mgPt cm⁻²</td>
<td>Fe-Cu-Ni/C</td>
<td>Tokuyama Asahi Glass Co.</td>
<td>25</td>
<td>4.3</td>
<td>8.6</td>
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<tr>
<td>AEMFC</td>
<td>1.0 M Glycerol 6.0 M KOH</td>
<td>Pt/C 1 mgPt cm⁻²</td>
<td>Fe-Cu-Ni/C</td>
<td>Tokuyama A-006</td>
<td>60</td>
<td>25</td>
<td>8.3</td>
<td>[32]</td>
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</table>
### Table 2.S3 continued

<table>
<thead>
<tr>
<th>AEMFC</th>
<th>.01 M Glycerol 1.0 M KOH</th>
<th>PtRu/C 4 mgPt + Ru cm⁻²</th>
<th>Pt/C 1 mgPt cm⁻²</th>
<th>Tokuyama AHA</th>
<th>50</th>
<th>6.8</th>
<th>1.16</th>
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</thead>
<tbody>
<tr>
<td>MFC</td>
<td>Crude glycerol Phosphate buffer solution</td>
<td>Pt/C 0.35 mgPt cm⁻²</td>
<td>-</td>
<td>25</td>
<td>0.211</td>
<td>0.63</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>MFC</td>
<td>Glycerol Phosphate buffer solution</td>
<td>Rhodopseudomonas palustris DX-1</td>
<td>Pt/C 0.5 mgPt cm⁻²</td>
<td>-</td>
<td>25</td>
<td>0.272</td>
<td>0.544</td>
<td>[25]</td>
</tr>
<tr>
<td>MFC</td>
<td>Glycerol Phosphate buffer solution</td>
<td>PQQ-ADH PQQ-AldDH</td>
<td>Pt/C</td>
<td>Nafion NRE212</td>
<td>25</td>
<td>1.32</td>
<td>[26]</td>
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<tr>
<td>MFC</td>
<td>Glycerol Phosphate buffer solution</td>
<td>PQQ-ADH PQQ-AldDH</td>
<td>Pt/C</td>
<td>TMOA modified Nafion</td>
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<td>1.21</td>
<td>[24]</td>
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<tr>
<td>MFC</td>
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<td>BBK006 Pt Wire</td>
<td>Pt</td>
<td>FAA</td>
<td>25</td>
<td>0.006</td>
<td>[28]</td>
<td></td>
</tr>
</tbody>
</table>

*PPD: Peak power density
**Unit: mW mg⁻¹ precious metal per MEA⁻¹

### 2.1.8 References


3.1 Metal-Catalyst-Free Carbohydrazide Fuel Cells with Three-Dimensional Graphene Anodes

3.1.1 Graphical abstract

Figure 3.1 Graphical abstract of section 3.1.

This section is adapted from a published paper (Ji Qi, Neeva Benipal, Hui Wang, David J. Chadderdon, Yibo Jiang, Wei Wei, Yun Hang Hu, Wenzhen Li, Metal-Catalyst-Free Carbohydrazide Fuel Cells with Three-Dimensional Graphene Anodes, ChemSusChem, 8 (2015) 1147-1150). Based on the high fuel cell performance baseline, this research focus on replacing metal catalysts with 3D carbon catalysts with large surface area. With carbon as active sites, the C-N of carbohydrazide bond can be cleaved.
### 3.1.2 Abstract

As a potential solution to sustainable energy concern, widespread commercialization of fuel cell has long been hindered by limited reserve and relatively high cost of metal catalysts. 3D graphene, a carbon-only catalyst prepared by reduction of carbon monoxide with lithium oxide, is found to electrochemically catalyze carbohydrazide oxidation reaction efficiently. Prototypes of anode metal catalyst free and completely metal catalyst free anion exchange membrane fuel cell with 3D graphene anode catalyst generate peak power density of 75.1 mW cm$^{-2}$ and 24.9 mW cm$^{-2}$, respectively. The average electron number electrochemically extracted from one carbohydrazide molecule is 4.9, indicating the existence of C-N bond activation, which is a key factor contributing to high fuel utilization efficiency.

### 3.1.3 Introduction

Precious metal catalyst, such as Pt, Pd, Au and Rh, is one of the most expensive components of low temperature fuel cell. To explore sustainable energy solution, there is an urgent need to design highly efficient and cost-effective catalytic materials for conversion of chemical energy stored in chemicals to electricity. So far, at the cathode side of low temperature fuel cells, the catalysts for oxygen reduction reaction (ORR) have been evolved from noble metal platinum to non-noble metal (Me) Me/N/C macrocycle composites[1-3], and finally to metal free nitrogen-doped carbons[4, 5]. At the anode side, research interest was first focused on the reduction in noble metal loading and later on their replacement with non-noble metal catalysts for electro-oxidation of hydrogen[6, 7], alcohol[8, 9], and hydrazine[10, 11]. Nevertheless, it is still very challenging to replace metal catalysts at the anode side of low
temperature fuel cells by non-metal catalysts, followed by achieving total removal of the metal catalysts from fuel cells.

Although served as metal free heterogeneous catalysts (carbocatalysis),[12, 13] carbon, which is inexpensive, abundant, and electro/chemically stable, has been only widely used as inert catalyst support in fuel cell anode for a long time. Since its discovery[14], graphene has been regarded as a rising star in varies of scientific and engineering area[15]. Aiming at developing complete metal catalyst free fuel cells, three-dimensional graphene (3D graphene) carbon material is proposed as a fuel cell anode catalyst for oxidation reaction. Since carbon is free from poisoning by many chemicals such as CO-like reaction intermediates and sulfur, fuel cell with graphene anode catalyst may utilize unpurified crude chemicals as fuel in the future. Moreover, the agglomeration issue of metal nanoparticles as fuel cell catalyst is also solved by adopting graphene carbon material.

So as to employ metal free graphene materials as fuel cell anode catalyst, an active fuel with strong reducing capability is required to ensure an oxidation reaction with sufficiently high thermodynamic electromotive force. As a high-energy molecule, hydrazine contains readily activated N-H bonds, rendering it a suitable potential fuel for anion exchange membrane fuel cells (AEMFCs) without noble metal catalyst. Specifically, nickel based anode catalysts dominate the state-of-the-art of low temperature direct hydrazine/oxygen fuel cells (Table 3.S1). Despite high reactivity, hydrazine’s high toxicity to central nerve system of human remains a real concern for its extensive applications. With a volumetric energy density of 4.2 kWh L⁻¹, carbohydrazide is a non-toxic alternative to hydrazine since the equilibrium electromotive force under standard condition of carbohydrazide/O₂ fuel cell (+1.65V)
calculated from thermodynamic data[16] is superior to those of hydrazine/O₂ (+1.62 V), ethanol/O₂ (i.e. <+1.17 V), and H₂/O₂ fuel cells (+1.23 V). (Table 3.1)

\[
\text{CH}_6\text{N}_4\text{O} + 8\text{OH}^- \leftrightarrow \text{CO}_2 + 7\text{H}_2\text{O} + 2\text{N}_2 + 8\text{e}^- \quad \text{E}^\circ = -1.25 \text{ V vs SHE} \quad (1)
\]

\[
2\text{O}_2 + 4\text{H}_2\text{O} + 8\text{e}^- \leftrightarrow 8\text{OH}^- \quad \text{E}^\circ = +0.40 \text{ V vs SHE} \quad (2)
\]

\[
\text{CH}_6\text{N}_4\text{O} + 2\text{O}_2 \leftrightarrow \text{CO}_2 + 3\text{H}_2\text{O} + 2\text{N}_2 \quad \text{E}^\circ = +1.65 \text{ V} \quad (3)
\]

Full oxidation of carbohydrazide generates 8 electrons per carbohydrazide molecule (Equation 1-3) with a thermodynamic efficiency of 95.6 % (Table 3.1).

**Table 3.1** Thermodynamic data of different oxygen based fuel cells

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Final Product</th>
<th>n[^{[a]}]</th>
<th>E[^{[b]}]</th>
<th>W[^{[c]}]</th>
<th>η[^{[d]}]</th>
<th>η[^{[e]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H₂O</td>
<td>2</td>
<td>1.23</td>
<td>2.6(liquid)</td>
<td>100</td>
<td>83.3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Acetic acid</td>
<td>4</td>
<td>1.17</td>
<td>2.1</td>
<td>33.3</td>
<td>91.8</td>
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<td>CO₂</td>
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<td>1.14</td>
<td>6.4</td>
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<td>Carbohydrazide</td>
<td>CO₂+N₂</td>
<td>8</td>
<td>1.65</td>
<td>4.2(solid)</td>
<td>100</td>
<td>95.6</td>
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</tbody>
</table>

\[^{[a]}\]n: number of electrons extracted from single reactant molecule; \[^{[b]}\]E\(_\text{0}\): equilibrium electromotive force under standard condition; \[^{[c]}\] W\(_\text{C}\): the volumetric density; \[^{[d]}\] η\(_\text{e}\): electron efficiency; \[^{[e]}\] η: thermodynamic efficiency \(\Delta G/\Delta H\).

Taking into account materials and reaction factors, metal catalyst free fuel cells were designed in the present work for exploiting three-dimensional graphene (3D graphene) anode catalyst with crater shaped projection for the electrocatalytic carbohydrazide oxidation reaction (CBOR). Among all tested samples, the 3D graphene exhibits the highest peak current density in a half cell as well as the highest peak power density (PPD) in the single cell. A prototype of
complete metal catalyst free AEMFC with the 3D graphene anode catalyst and nitrogen-doped carbon nanotube (N-CNT) cathode catalyst was demonstrated afterwards.

3.1.4 Experimental section

**Chemicals:**

XGnP Graphite NanoPlatelets (2D graphene) were purchased from XG sciences, Inc. The nitrogen doped carbon nanotubes (N-CNT) were gained from NanoTechLabs. Inc. (NTL). Carbohydrazide (98%), benzaldehyde (99.5%), polytetrafluoroethylene water solution (60%), potassium hydroxide (85%), potassium phosphate monobasic (>99%) and 1-propanol (99.5%) were obtained from Sigma-Aldrich Co. The catalyst 4020 was bought from Acta, Inc.

**Preparation of 3D graphene with Li$_2$O and CO:**

3D graphene was synthesized through a method[17] based on the reaction between Li$_2$O and CO. 1.0 mol of lithium oxide (Li$_2$O) powder was treated with CO in a batch ceramic-tube reactor. The pressure and temperature were kept at 35 psi and 550 °C for 12 h, respectively. The products were treated with diluted hydrochloric acid for more than 10 times to remove Li$_2$O, Li$_2$CO$_3$ and impurities. The final product, 3D graphene with crater shaped projections, was obtained by filtrating, washing with distilled water and drying at 80 °C overnight.

**Physical characterizations for comparing morphology and detecting residual elements:**

The field emission scanning electron microscope (FESEM) image of 3D graphene and transmission electron microscopy (TEM) images of 3D graphene, 2D graphene and N-CNT
were collected on Hitachi-4700 under 5kV operating voltage and JEOL JEM-4000FX under 200 kV operating voltage, respectively. The sample ink concentration was as low as 3 mg ml\(^{-1}\) so as to alleviate agglomeration and packing of carbon materials on the microscopy sample supporting substrate.

The iron amount in N-CNT before and after acid treatment was characterized by inductively coupled plasma optical emission spectrometry (ICP-OES). The samples were dissolved in aqua regia by ultra-sonication for 1 h. After standing overnight to promote Fe ionization, the samples were diluted to < 10 ppm and then filtrated to remove N-CNT before Fe quantification. The ICP-OES results show the Fe amount in the N-CNT decreases from 5.6 wt% to <0.08 wt% (close to detection limit) after the hydrochloric acid purification. The polarization and power density curves of the single direct carbohydrozide fuel cells with the 3D graphene anode and N-CNT before and after acid treatment are shown in Figure 3.S4.

**Cyclic voltammetry tests demonstrating the activity of 3D graphene towards CBOR:**

The cyclic voltammetry (CV) was performed using 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). All experiments were performed at ambient temperature under nitrogen blanket to avoid introducing oxygen to the system. The glassy carbon electrode (GCE) was polished with alumina micro polish solution and grinding paper to avoid contaminations. The catalyst ink with a concentration of 1.0 mg ml\(^{-1}\) was acquired by ultrasonically treating a mixture of 2.7 ml 1-propanol and 2.7 mg catalysts in ice-water bath with shaking for 2-3 minutes to obtain
uniform ink. 20 uL of the catalyst ink was evenly syringed dropwise onto the surface of GCE. The mixture of 1.0 M potassium hydroxide (KOH) and 0.1 M carbodihydrazide (\(\text{CH}_6\text{N}_4\text{O}\)) was prepared as fuel right before the experiment started. The scan rate was kept at 50 mV s\(^{-1}\) for CV test.

**Single-cell tests for anode metal free and metal free fuel cells:**

The polarization curves and power density curves were obtained by using a fuel cell system (850e Scribner-Associates) with self-made membrane electrode assembly (MEA), serpentine graphite flow field plate, and feedback temperature control loop composed of electric heating rods and thermocouple thermometer. The MEA with an active area of 5 cm\(^2\) was composed of carbon cloth as anode catalyst substrate, anion exchange membrane (A901 Tokuyama, 10 µm) as cathode catalyst substrate and carbon paper as cathode backing layer. Utilizing 1-propanol as solvent and 5% polytetrafluoroethylene (PTFE Teflon) as binder (catalyst: PTFE=8:2 mass ratio), the anode catalyst ink with a concentration of 10 mg cm\(^{-3}\), was ultra-sonicated in an ice-water bath for 40 min to ensure uniform dispersion. The anode catalyst substrate was prepared by spraying catalyst ink onto carbon cloth with catalyst loading of 10 mg cm\(^{-2}\) 2D graphene and 3D graphene. The cathode catalyst substrate was constructed by spraying 1 mg cm\(^{-2}\) non-noble metal loading commercial catalyst (4020 Acta or N-CNT) with a ratio of 7:3 an ionomer (AS-4 Tokuyama) onto an anion exchange membrane (A901 Tokuyama). The N-CNT was treated by 3.0 M hydrochloric acid in ultrasonic water bath with stirring for 24 h to remove the residual iron and then fully rinsed with de-ionized water.
HPLC analysis of carbohydrazide conversion:

Carbohydrazide was quantified using a modified precolumn derivatization method[18]. To prepare the mobile phase, 13.75g of potassium phosphate monobasic (KOH2PO4) was dissolved in 1000 ml deionized water. Once the solution was well mixed; the pH was changed to 7 by adding additional 1.0 M KOH dropwise. Then, 550 ml of the above solution was diluted with 450 ml of acetonitrile; followed by filtration and sonication.

Samples containing carbohydrazide derivatives were analyzed using HPLC (Agilent 1100) with a refractive-index detector (RID, Agilent G1326A), a variable wavelength detector (VWD, 220 nm, Agilent) and a SphereClone ODS (1) column (Phenomenex 100 x 4.6 mm). The mobile phase flow rate was 0.4 ml min⁻¹ while the column temperature was 60 °C. The amount of carbohydrazide consumed by electrochemical reactions was obtained by comparison with the results from a control experiment where only non-electrochemical reactions occurred, i.e. open-circuit fuel cell operation. Since highly active carbohydrazide may undergo some chemical reactions, the experiment is time sensitive. Hence, to ensure reproducibility, it was necessary to apply an integrated fuel cell testing and analysis procedure. Briefly, raw, control and reacted samples were collected in sequence. Raw sample was collected directly from 6.0 M KOH and 1.0 M carbohydrazide fuel. Control and reacted samples were obtained from the fuel cell outlet after a single pass through the cell, without and with starting the fuel cell experiment, respectively. Each sample was neutralized with mobile phase before being derivatized with 15 wt% benzenaldehyde solution. A sample volume of 20 µL was injected into the HPLC system for analysis.

The average number of electrons transferred per carbohydrazide molecule in the electrochemical CBOR was calculated according to:
\[ n = \frac{Q}{mF} = \frac{\int_{t_1}^{t_2} Idt}{v(t_2 - t_1)(C_b - C_r)F} \]

where \( n \) is the average electrons transferred in the electrochemical CBOR; \( Q \) is the actual charge integrated from \( I-t \) curve (Figure 3.3d); \( m \) is the molar amount of carbohydrazide consumed in the electrochemical CBOR; \( t_1 \) and \( t_2 \) are the reaction time bounds for integration \((t_1 = 3 \text{ min}, t_2 = 6 \text{ min})\); \( I \) is instantaneous cell current; \( v \) is the volumetric flow rate of fuel \((1 \text{ ml min}^{-1})\); \( C_b \) and \( C_r \) are the carbohydrazide concentrations in blank (control) and reacted samples respectively; \( F \) is Faraday’s constant.

3.1.5 Results and discussion

**Figure 3.2** Bright field transmission electron microscopy (TEM) images of 3D graphene treated with a) diluted hydrochloride acid and b) concentrated hydrochloride acid. Dark field TEM images of c) 3D graphene and d) enlarged local area.
As shown in Figure 3.1a, the crater-structured nanoscale cells on 3D graphene protrude from the basal plane, thereby increasing the surface area of each single graphene sheet. The 3D graphene (Figure 3.1a) greatly differs from graphene nanoplatelets with a flat micro-scale 2D structure (Figure 3.1S1). Moreover, by comparing Figure 3.1a and Figure 3.1b, it can be concluded that diluted hydrochloric acid maintains the dedicated crater shaped projections on 3D graphene and avoid agglomeration while concentrated hydrochloric acid does the opposite things. The diameter of these crater shaped projections further highlighted by dark field TEM (Figure 3.1c and Figure 3.1d) is measured to be between 60 nm to 150 nm while the thickness of them ranges from 7 nm to 20 nm.

![Cyclic voltammograms of 3D graphene, 2D graphene and glassy carbon for carbohydrazide oxidation in N₂ purged 1.0 M KOH + 0.1 M carbohydrazide at 50 mV s⁻¹ under RT.](image)

**Figure 3.3** Cyclic voltammograms of 3D graphene, 2D graphene and glassy carbon for carbohydrazide oxidation in N₂ purged 1.0 M KOH + 0.1 M carbohydrazide at 50 mV s⁻¹ under RT.

Cyclic voltammetry results show that carbon is active towards CBOR (Figure 3.2). The activity sequence is 3D graphene (20.1 mA cm⁻² and -0.42 V) > 2D graphene (10.2 mA cm⁻² and -0.32 V) > glassy carbon (6.1 mA cm⁻² and -0.21 V) in terms of peak current density and
onset potential, due to different catalyst layer structures of 3D graphene (3D microscale catalyst layer with nanoscale cells), 2D graphene nanoplatelets (microscale flat surface) and glassy carbon electrode (bulk flat surface).

**Figure 3.4** a) Polarization and power density curves of anode metal catalyst free direct carbohydrazide AEMFC with different anode carbon catalyst. Anode fuel: 6.0 M KOH, 1.0 M carbohydrazide, 4.0 ml min\(^{-1}\); temperature (anode fuel/cathode fuel/cell): 25/80/80 °C . b) Ohmic resistance of fuel cell corresponding to Figure 3.3a. c) Polarization and power density curves of AEMFC with 3D graphene anode catalyst operated under different concentration of KOH. d) Chronoamperometry curve for analysis of the average number of electrons electrochemically extracted per carbohydrazide molecule during carbohydrazide oxidation reaction (CBOR) catalyzed by 3D graphene anode catalyst in AEMFC. Anode fuel: 6.0 M KOH + 1.0 M carbohydrazide, 4.0 ml min\(^{-1}\); Cell voltage: 0.25 V; cell temperature: 60 °C. Other testing conditions for all the experiments above: Anode catalyst loading: 5 mg\textsubscript{catalyst} cm\(^{-2}\); Cathode catalyst: Fe-based catalyst (Acta 4020, 3 mg cm\(^{-2}\)); AEM: Tokuyama A901; cathode fuel: 200 ml min\(^{-1}\) O\(_2\), ambient pressure.

The prototype of an anode metal catalyst free AEMFC was demonstrated by combining anode metal free carbon catalyst and cathode noble metal free Fe-based catalyst (Acta 4020) catalyst (Figure 3.3a). The open circuit voltage (OCV) of the direct carbohydrazide AEMFC
with the 3D graphene anode catalyst was 0.594 V, which is 21 mV higher than that with 2D graphene (0.573 V) and 41 mV higher than that with carbon cloth blank substrate (0.553 V). The PPD of the direct carbohydrazide AEMFC with the 3D graphene anode catalyst was 75.2 mW cm\(^{-2}\), which is 78 % higher than that with 2D graphene and 5.9 times that with blank carbon cloth substrate. The consistent results shown in both half cell and single cell tests reveal the mass activity sequence toward CBOR for direct carbohydrazide AEMFC as 3D graphene > 2D graphene > bulk carbon substrate (glassy carbon or carbon cloth), which can mainly be attributed to two factors: catalytic activity (associated with surface area and electrode structure) and electronic conductivity. The specific surface area of 3D graphene (151 m\(^2\) g\(^{-1}\)) is larger than that of 2D graphene (125 m\(^2\) g\(^{-1}\)). Additionally, the projections on 3D graphene function as spacers to form a 3D electrode structure, leading to an even greater number of catalytically active sites for CBOR. The IR (Figure 3.3b) of 3D graphene based anode metal catalyst free fuel cell (10 mΩ) was lower than that of 2D graphene (16 mΩ) and carbon cloth substrate (70 mΩ), indicating higher electrical conductivity of 3D graphene, which gave rise to the higher performance for 3D graphene-based anode metal catalyst free fuel cell, especially when compared with the performance for the carbon fiber cloth substrate based anode.

The performance of anode metal catalyst free direct carbohydrazide AEMFC was also dependent on KOH concentration (Figure 3.3c). Cell voltage increased with increasing KOH concentration over all current regions up to 6.0 M KOH, but further increasing KOH concentration to 9.0 M resulted in fuel cell performance drop. This trend is attributed to the balance between facilitated deprotonation of carbohydrazide by higher KOH concentration and the reverse-parabolic relationship between KOH concentration and the IR of the fuel cell. When KOH concentration increases from 0 M to 12.0 M at 60 °C, the corresponding electrical
conductivity of the KOH water solution reaches a maximum at 6.0–7.0 M\textsuperscript{[19]}, resulting in a reverse-parabolic trend of IR with KOH concentration (Figure 3.S2).

Fuel utilization efficiency for the CBOR were evaluated after verifying the feasibility of anode metal catalyst free fuel cell. Unlike hydrazine, the carbohydrazide molecule has two C-N bonds and a C=O bond, in addition to N-H and N-N bonds. Cleavage of C-N bonds is essential for complete oxidation of carbohydrazide, achieving optimal fuel utilization efficiency. The fuel utilization efficiency can be reflected by average electron number of electrons transferred per carbohydrazide molecule, which is determined by carbohydrazide conversion and total charge transfer in the electrocatalytic CBOR. To evaluate the conversion of carbohydrazide in the electrocatalytic CBOR, the AEMFC anode outlet stream was analyzed by HPLC. Additionally, the corresponding cell current was integrated over time to obtain the total charge transferred. In Figure 3.3d, the shaded area is equal to the total charge (1.93 C) transferred during electrochemical CBOR, integrated from 3 to 6 min.

For anode metal catalyst free direct carbohydrazide fuel cell with 3D graphene anode catalyst, the average electron number of electrons transferred per carbohydrazide molecule was 4.9, leading to a 61.25 % electron efficiency with respect to complete oxidation of carbohydrazide (Equation 1). The existence of parallel reaction pathways, including both partial and complete oxidation, can thus be confirmed. However, taking into account the electrochemical promotion effect of chemical catalytic reactions ("EPOC")\textsuperscript{[20-22]}, the real non-faradaic reaction rate was likely faster in the electrocatalytic operation than in the control experiment (only carbohydrazide chemical oxidation). Therefore, the actual number of electrons transferred in the electrochemical CBOR should be higher than this apparent value, which strongly suggests that nano-carbon itself facilitates deep oxidation of carbohydrazide.
After confirming the feasibility of anode metal catalyst free fuel cell and the corresponding fuel utilization efficiency, a complete metal catalyst free direct carbohydrazide AEMFC (Figure 3.4a) was established by combining 3D graphene as catalyst for CBOR at the anode side, A901 AEM as hydroxide ion conductor in the center and N-CNT as catalyst for
ORR at the cathode side. The AEM-based metal catalyst free fuel cell achieved a PPD of 24.9 mW cm$^{-2}$ (Figure 3.4b). For comparison, a H$_2$-AEMFC with Ni-Cr anode catalyst and Ag cathode catalyst has been developed generating a PPD of 50 mW cm$^{-2}$.[6] Direct alcohol AEMFC with Fe-macrocycle cathode catalyst has also shown promising PPD [23-25]. However, Fe, Ni, Cr, Ag metals were still used in the anode and cathode for electro-oxidation of fuels and ORR. Although the PPD is lower than that of Pt-based proton exchange membrane fuel cell, this metal catalyst free AEMFC is proposed as one option for the future form of fuel cell. Furthermore, it should be noted that 99.99% purity oxygen was applied at the cathode in this work. When more ubiquitous CO$_2$-containing air is used, a potential concern regarding carbonate precipitation should be considered. Fortunately, this issue could be alleviated by absorbing CO$_2$ in the air with used anode fuel containing excessive KOH solution. Alternatively, removing liquid KOH from current fuel cell system is another potential solution.

3.1.6 Conclusions

In summary, novel anode metal catalyst free and complete metal catalyst free direct carbohydrazide AEMFCs with 3D graphene anode catalyst have been successfully developed in this work, which opens a new research arena for exploring electrocatalytic properties of advanced nano-carbon materials and developing inexpensive fuel cells. Future research efforts such as modifying nanocarbon catalysts in order to reduce over-potential, inhibiting non-faradaic carbohydrazide oxidation reaction, extracting more electrons from the electrocatalytic CBOR, and minimizing liquid base should be made to improve the feasibility of current metal catalyst free fuel cell technology.
### 3.1.7 Supporting information

#### Table 3.S1 State-of-the-art of low temperature direct hydrazine/oxygen fuel cells

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<th>Cathode catalyst</th>
<th>Electrolyte</th>
<th>Temperature (°C)</th>
<th><em>PPD</em> (mW cm(^{-2}))</th>
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<td>Ni</td>
<td>NiZn</td>
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<td>80</td>
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<td>NiLa</td>
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<td>459</td>
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<td>Co based catalyst</td>
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<td>20 vol% N(_2)H(_4)•H(_2)O</td>
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<td>NiLa</td>
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<td>46</td>
<td>[29]</td>
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<td>5 wt% N(_2)H(_4)•H(_2)O</td>
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<td>Co/C</td>
<td>QPE based AEM</td>
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<td>CoNₓ/C</td>
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*PPD: Peak power density

Figure 3.S1. Transmission electron microscopy (TEM) image of 2D graphene.
Figure 3.S2 Average ohmic resistance of fuel cell corresponding to Figure 3.3c.

Figure 3.S3 Polarization and power density curves of AEMFC with 3D graphene anode catalyst operated under different temperature. Anode fuel: 6.0 M KOH, 1.0 M carbohydrazide, 4.0 ml min⁻¹.
Figure 3.4. Polarization and power density curves of metal catalyst free direct carbohydrazide AEMFC (catalyst before and after acid treatment) with 3D graphene anode catalyst (5 mg_{catalyst} cm^{-2}); AEM: Tokuyama A901; cathode catalyst (1.0 mg_{catalyst} cm^{-2}): N-CNT; anode fuel: 6.0 M KOH, 1.0 M carbohydrazide, 4.0 ml min^{-1}; cathode fuel: 200 ml min^{-1} O_2, ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/80/80 °C.

Figure 3.3 shows the polarization and power density curves of direct carbohydrazide AEMFC with 3D graphene anode catalyst operated at different temperatures. The OCVs of the anode metal catalyst free direct carbohydrazide AEMFC operating at 25, 40, 60, and 80 °C were 0.54, 0.56, 0.58, and 0.59 V, while PPD were 27.0, 36.6 and 75.2 mW cm^{-2}, respectively.

3.1.8 References


3.2 Carbon Nanotubes as Catalysts for Direct Carbohydrazide Fuel Cells

3.2.1 Graphical abstract

![Graphical abstract of section 3.2.](image.png)

**Figure 3.6** Graphical abstract of section 3.2.

This section is adapted from a published paper (Ji Qi, Neeva Benipal, David J. Chadderdon, Jiajie Huo, Yibo Jiang, Yang Qiu, Xiaotong Han, Yun Hang Hu, Brent H. Shanks, Wenzhen Li, Carbon nanotubes as catalysts for direct carbohydrazide fuel cells, Carbon, 89 (2015) 142-147). With CNT as anode catalyst, this research focus on increasing the surface area of the anode electrode with a 3D electrode structure.
3.2.2 Abstract

As an alternative to potentially carcinogenic hydrazine for fuel cell application, carbohydrazide, which contains lone electron pairs on nitrogen atoms and readily activated N-H bonds, can be catalytically oxidized over metal-free carbon catalysts due to the high equilibrium electromotive force (1.65 V) of its oxidation reaction. Carbon nanotubes are found to electrochemically catalyze the carbohydrazide oxidation reaction more efficiently than carbon black and multi-layer graphene in alkaline media. With carbon nanotubes as the anode catalyst, anode metal-catalyst-free and completely metal-catalyst-free direct carbohydrazide anion exchange membrane fuel cells are shown here to generate a peak power density of 77.5 mW cm\(^{-2}\) and 26.5 mW cm\(^{-2}\), respectively.

3.2.3 Introduction

As an abundant, stable and low-cost material, carbon is an ideal non-metal candidate for fuel cell electrocatalysts. For the realization of a low-temperature fuel cell with metal-free catalysts, active chemicals have to be adopted to overcome the overpotential barrier and thus increase the cell operating voltage. Carbohydrazide, a high energy density (4.16 kWh/L) hydrazine derivative containing a readily activated N-H bond, is a non-toxic alternative to hydrazine, and can potentially be fully oxidized to non-toxic nitrogen, water and carbon dioxide, releasing eight electrons per molecule. In acid electrolyte[1], nitrogen serves as the main product for carbohydrazide oxidation reaction (CBOR) on the platinum electrode for the reason that the stable N-N bond prevents generation of detectable toxic cyanamide and cyanate. Similarly in alkaline medium[2], the N-N bond is hard to cleave on various kinds of mono-
metallic electrodes, such as Pt, Au, Ag, Fe, Co, Ni, and Cu. Moreover, the relatively high thermal-equilibrium potential (+1.65 V) of a direct carbohydrazide fuel cell at standard conditions effectively counteracts the overpotential of electrocatalytic CBOR.

In the present work, the feasibility of a novel direct carbohydrazide fuel cell powered by carbon catalysts is shown. Carbon nanotubes (CNT) outperform carbon black (CB) and multi-layer graphene (MLG) for the anodic CBOR. An anode metal-catalyst-free direct carbohydrazide anion exchange membrane fuel cell (AEMFC) with a CNT anode catalyst and a Fe-based cathode catalyst generates a peak power density of 77.5 mW cm\(^{-2}\) at 80 °C, while a completely metal-catalyst-free cell with a CNT anode catalyst and a nitrogen-doped CNT (N-CNT) cathode catalyst generates a peak power density of 26.5 mW cm\(^{-2}\).

3.2.4 Experimental section

Chemicals:

The short multi-walled CNT (8-15 nm outer diameter, 0.5-2 μm length), bought from Cheaptubes Inc., were grown by combustion chemical vapor deposition (CCVD) method and acid purified. They were subsequently shortened using an extrusion system.

XGnP MLG, Vulcan XC-72R CB and N-CNT were purchased from XG sciences, Inc., Fuel Cell Store and Nano Tech Labs. Inc. (NTL), respectively. Carbohydrazide (98%), polytetrafluoroethylene water solution (60%), potassium hydroxide (85%) and 1-propanol (99.5%) were obtained from Sigma-Aldrich Co. The catalyst 4020 was bought from Acta, Inc.
Transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) surface area, and thermogravimetric analysis (TGA) physical characterizations:

TEM images of the CNT, CB and MLG were obtained on a JEOL 2010, operated at a voltage of 200 kV. Before dropwise addition onto the copper grid support with carbon film, the samples were well-dispersed ultrasonically in methanol. BET surface area was determined by N₂ physisorption in a Micromeritics ASAP 2020 after a degassing process. Thermal gravimetric analysis (TGA) was performed in a Perkin Elmer STA 6000 Simultaneous Thermal Analyzer with a temperature ramp of 10 K/min and an air flow of 20 ml/min.

Acid purification of CNT and N-CNT and their inductively coupled plasma optical emission spectrometry (ICP-OES) characterization:

The CNT and N-CNT were ultrasonicated in 3.0 M hydrochloric acid with mechanical stirring for 12 hours, followed by rinsing with 6 L de-ionized water. After this process was repeated, the CNT and N-CNT were dried in a vacuum oven for 12 hours. For ICP-OES analysis, the CNT and N-CNT were dissolved in aqua regia with ultra-sonication for 1 h, followed by standing overnight to promote Fe ionization. The samples were diluted to < 10 ppm and then filtrated to remove carbon before Fe quantification.

Electrochemical characterization in three electrode half cell system and membrane electrode assembly based single cell system:

The cyclic voltammetry (CV) was conducted in 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). 2.7 mg catalyst was dispersed in 5.4 mL 1-propanol by continuously shaking the container in an ultrasonic ice-water bath for 2 min to obtain a uniform black colored catalyst ink with a concentration of 0.5 mg mL$^{-1}$. 20 μL of the catalyst ink was added dropwise onto the surface of the glassy carbon electrode (GCE) with a glass syringe. The electrolyte was composed of 1.0 M potassium hydroxide (KOH) and 0.1 M carbohydrazide (CH$_6$N$_4$O). The CV tests were executed at room temperature under nitrogen protection with a scan rate of 50 mV s$^{-1}$.

The current, potential and power density raw data were collected under ambient pressure and at various temperatures on a fuel cell test stand (850e Scribner-Associates) connected with a single cell module including a self-made membrane electrode assembly (MEA), two serpentine graphite flow field plates, two glided plate-shaped current collectors and feedback temperature control loop composed of electric heating rods and thermocouple thermometer. The 5 cm$^2$ MEA was assembled by combining the anode catalyst substrate (carbon cloth), the cathode catalyst substrate integrated with membrane (A901 anion exchange membrane Tokuyama, 10μm) and the cathode backing layer (carbon paper). The anode catalyst ink, using 1-propanol as solvent and 5% polytetrafluoroethylene (PTFE Teflon) as binder (catalyst: PTFE=8:2 mass ratio), was ultra-sonicated in an ice-water bath for 40 min to ensure uniform dispersion even under a relatively high ink concentration of 10 mg cm$^{-3}$. The catalyst loading on the anode catalyst substrate was controlled to 10 mg cm$^{-2}$ by gradually spraying catalyst ink onto the carbon cloth. The cathode catalyst substrate was made by spraying 1 mg cm$^{-2}$ of the cathode catalyst (4020 Acta or N-CNT) onto an anion exchange membrane (A901 Tokuyama). The cathode catalyst ink was prepared similarly as the anode catalyst ink with 30 wt% of ionomer (AS4 Tokuyama) as binder and anion conductor. The default testing condition
was anode fuel: 6.0 M KOH, 1.0 M carbohydrizide, 4.0 ml min⁻¹; cathode fuel: 200 ml min⁻¹ O₂, ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/80/80 °C.

3.2.5 Results and discussion

Figure 3.7 Morphology comparison based on TEM images of a) MLG b) CB (Vulcan XC-72R) c) CNT and d) N-CNT.

Table 3.2 Summarization of physical characterizations for carbon materials

<table>
<thead>
<tr>
<th>Carbon samples</th>
<th>Diameterᵃ (nm)</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Thermally unstable temperature in airᵇ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLG</td>
<td>&gt;1000</td>
<td>125</td>
<td>201</td>
</tr>
<tr>
<td>CB</td>
<td>20-50</td>
<td>254</td>
<td>&gt;400</td>
</tr>
<tr>
<td>CNT</td>
<td>8-15 (length: 0.5-2µm)</td>
<td>233</td>
<td>275</td>
</tr>
<tr>
<td>N-CNT</td>
<td>20-40 (length: ~50µm)</td>
<td>124</td>
<td>&gt;400</td>
</tr>
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</table>

ᵃ. Outer diameter for CNT and N-CNT; particle diameter for CB; cluster diameter for MLG
ᵇ. The temperature when a carbon sample loses 0.5 wt% of its original weight in TGA experiments
The MLG have a μm-scale two-dimensional structure (diameter > 1 μm) with a flat surface (Figure 3.5a), leading to a BET surface area (125 m² g⁻¹) lower than that of CB (254 m² g⁻¹) and CNT (233 m² g⁻¹). When MLG is fabricated into an electrode, only the surface layers are exposed to the electrolyte, leading to a remarkable amount of graphite layers buried underneath, which are inaccessible to the electrocatalytic CBOR. The CB (Vulcan XC-72R) has a much smaller diameter than that of MLG. It can form a nm-scale rough surface when piled as catalyst layer on the electrode, enabling a higher graphite layer utilization. When the 1-D CNTs formed random agglomeration in the catalyst layer, there is significant interspace formed between them, which provides the entire CNT-based electrode with a three-dimensional (3D) structure. Since the diameter of the CNT is only 8-15 nm, the 3D network electrode structure will ensure colossal nano-scale exposure of carbon surface to electrolyte. Despite the large BET surface area determined by gas physical adsorption, the CB has more nm-scale pores on its surface, which will likely lead to more mass transfer issues for CBOR compared with CNT. Therefore, the CNT’s actual carbon surface utilization for CBOR can still be higher than that of Vulcan XC-72R. All the carbon materials are thermally stable (Table 3.2) in air for low-temperature anion exchange membrane fuel cell (25-90 °C).
As an azotic ligand with lone pairs of electrons with strong reducing ability [3], carbohydrazide has been proven to be electrochemically active on metal-based structures [2, 4]. To evaluate the electrocatalytic activity of carbon towards carbohydrazide oxidation reaction (CBOR), cyclic voltammetry was conducted in three electrodes system with CNT, CB and MLG as catalyst on the working electrode, respectively (Figure 3.6). The current density at 0.2 V for CNT (93.5 mA cm$^{-2}$) is 1.3 times that of CB (74.1 mA cm$^{-2}$), 3.8 times that of MLG (19.6 mA cm$^{-2}$) and 12.2 times that of blank glassy carbon electrode (7.1 mA cm$^{-2}$), which is attributed to the aforementioned catalyst layer structure difference of CNT (nano-scale 3D network), CB (nano-scale rough surface), MLG (micro-scale flat surface), and blank glassy carbon electrode (bulk flat surface). Due to a compromise between a small particle effect and the 3D network structure effect, the onset potential of the CBOR occurred on CB electrode (-0.440 V) is close to the counterpart for CNT (-0.420 V). With a micro-scale flat surface, the
onset potential of MLG (-0.320 V) is 120 mV and 100 mV more positive than that of CB and CNT, respectively, making the dimension of catalyst a determining factor for the mass activity of carbon catalyzed CBOR in alkaline media.

Figure 3.9 I-V polarization and power density curves of AEMFCs with carbon anode catalyst and Fe-based Acta 4020 cathode catalyst (a-c), a) comparison of different carbon material as anode catalyst; b) temperature effects c) KOH concentration effect and d) completely metal-catalyst-free AEMFC with CNT anode and N-CNT(before or after acid cleaning) cathode catalyst. O₂ is fed to cathode at ambient pressure.

Low-temperature AEMFC is adopted here as a promising platform to develop fuel cells with metal-free catalysts since reaction kinetics can be improved at both anode and cathode as a result of enhanced charge and ion transfer in high pH media. Figure 3.7a-c depicts the AEMFC performance with anode metal-free carbon catalyst and cathode noble metal-free Fe-based (Acta 4020) catalyst, confirming the overpotential of CBOR on carbon anode catalysts is also low enough to actually generate electricity in AEMFC. As demonstrated in Figure 3.7a, the open circuit voltage (OCV) of the direct carbohydrazide AEMFC with CNT as the anode
catalyst is 0.630 V, which is 31 mV, 57 mV and 86 mV higher than that with CB, MLG and carbon cloth substrate, respectively. Comparable to the performance of H$_2$-AEMFC with the Ni-Cr anode catalyst and Ag cathode catalyst (50 mW cm$^{-2}$)[5], the peak power density (PPD) of the direct carbohydrazide AEMFC with CNT as the anode catalyst is 77.5 mW cm$^2$, which is 11.8 % higher than that with CB (69.3 mW cm$^2$), 86.7 % higher than that with MLG (42.2 mW cm$^2$), and 5.4 times that with the blank carbon cloth substrate (12.2 mW cm$^2$). Ideally, the BET surface area of carbon materials measured by gas adsorption should be proportional to the active sites exposed to electrolyte catalyzing carbohydrazide oxidation. As far as the performance of direct carbohydrazide fuel cell with CNT and MLG anode catalysts is concerned, the peak power density (77.5 mW cm$^2$ and 42.2 mW cm$^2$) of the AEMFCs is proportional to the BET surface area of the anode catalysts (233 m$^2$ g$^{-1}$ and 125 m$^2$ g$^{-1}$), which is not the case as for CB. The CB has more pores [6] on its surface than CNT and MLG do, so some of its active sites’ effectiveness towards catalyzing carbohydrazide oxidation reaction is undermined by mass transfer issue. According to consistent results shown in both half cell and single cell tests, the mass activity sequence toward CBOR for direct carbohydrazide AEMFC application is CNT (8-15 nm) > CB (30-40 nm) > MLG (>1 μm) > bulk carbon substrate (glassy carbon or carbon cloth).

Figure 3.7b shows the polarization and power density curves of direct carbohydrazide AEMFC with the CNT anode catalyst operated under different temperatures. The OCV of the anode metal-catalyst-free direct carbohydrazide AEMFC operating at 25 ºC, 40 ºC, 60 ºC and 80 ºC is 0.53 V, 0.58 V, 0.61 V and 0.63 V, while PPD is 23.9 mW cm$^2$, 38.7 mW cm$^2$, 64.9 mW cm$^2$ and 77.5 mW cm$^2$ respectively. Higher fuel cell performance can be traced back to enhanced carbohydrazide oxidation kinetics offered by elevated temperature.
As shown in Figure 3.7c, the cell voltage first increases with KOH concentration up to 6.0 M and then decreases upon further concentration increases to 9.0 M. As a major factor affecting the AEMFC performance[7, 8] and product distribution[9], KOH concentration has a similar parabolic relationship with single cell PPD in direct ethanol [7] and glycerol [8] AEMFC, indicating the existence of common effects. Higher KOH concentration facilitates the deprotonation of carbohydrazide and thus enhances the kinetics of carbohydrazide oxidation. Meanwhile, boosted competitive adsorption between carbohydrazide and hydroxyl ion leads to a shortage of carbohydrazide on the catalyst surface. The tradeoff between enhanced kinetics and competitive adsorption has a direct association with the existence of optimized KOH concentration. Moreover, the internal resistance, which will first decrease and then increase as KOH concentration increases [8], is also responsible for the volcano type relationship between KOH concentration and single cell performance.

Figure 3.7d presents the performance of total metal-catalyst-free direct carbohydrazide AEMFC, in which the cathode Fe-based Acta 4020 catalyst was replaced by N-CNT. It’s reported that the residual metal on CNT has remarkable effects on biological[10] and electrochemical reactions[11]. Therefore, it is important to determine the dominant catalytic material in the current fuel cell. After purifying the anode CNT and cathode N-CNT catalyst by ultrasonication with 3.0 M hydrochloric acid (non-oxidizing acid to protect the carbon shell), the performance of the single cell before and after such process is compared, since residual Fe metal may also contribute to CBOR or ORR. By conducting hydrochloric acid treatment, the Fe amount detected by ICP-OES in anode CNT decreased from 0.019 wt% to 0.007 wt% (0.7 µgFe cm⁻²), while that in the cathode N-CNT decreases from 5.6 wt% to 0.079 wt% (7.9 µgFe cm⁻²). The one to two magnitude drop of the residual metal amount in CNT
and N-CNT confirms the effectiveness of the purification process. The OCV before acid treatment is 39 mV larger than that after acid treatment while the PPD of the former MEA (26.5 mW cm\(^{-2}\)) is just 0.9 mW cm\(^{-2}\) higher than that of the latter MEA (25.6 mW cm\(^{-2}\)). The metal-catalyst-free fuel cell with a MEA composed of acid purified catalysts performs similarly in electricity generation compared to one with an MEA composed of non-purified catalysts, indicating the dominant effective catalytic material is carbon rather than metal. Another reason for carbon atoms as proposed active sites is that the lone pairs of electrons make nitrogen atoms easily adsorbed. The target reaction mechanism is complete electrocatalytic oxidation of carbohydrazide with C-N bond cleavage, releasing 8 electrons per molecule:

\[
\text{CH}_6\text{N}_4\text{O} + 8\text{OH}^- \rightarrow \text{CO}_2 + 7\text{H}_2\text{O} + 2\text{N}_2 + 8\text{e}^- \quad E^o = -1.25 \text{ V vs SHE (1)}
\]

\[
2\text{O}_2 + 4\text{H}_2\text{O} + 8\text{e}^- \rightarrow 8\text{OH}^- \quad E^o = +0.40 \text{ V vs SHE (2)}
\]

\[
\text{CH}_6\text{N}_4\text{O} + 2\text{O}_2 \rightarrow \text{CO}_2 + 3\text{H}_2\text{O} + 2\text{N}_2 \quad E^o = +1.65 \text{ V (3)}
\]

However, due to high activity of carbohydrazide, chemical decomposition to hydrogen is possible, which has already been reported for hydrazine [12]. Therefore, designing more active catalytic materials as well as suppressing the chemical decomposition of carbohydrazide in alkaline media can further increase the efficiency of the fuel cell.

3.2.6 Conclusions

In summary, we have demonstrated CNT as an active carbon-based catalyst for anode metal-catalyst-free and completely metal-catalyst-free direct carbohydrazide AEMFC. Owing to its 3D catalyst layer structure, CNT is superior to CB and MLG and towards CBOR in half cell and single cell. With CNT as anode catalyst, the PPD under optimized KOH concentration and temperature of the anode metal-catalyst-free direct carbohydrazide AEMFC with Fe-based
cathode catalyst is 77.5 mW cm\(^{-2}\), while the counterpart of completely metal-catalyst-free direct carbohydrazide AEMFC with N-CNT cathode catalyst is 26.5 mW cm\(^{-2}\). Carbon materials with relatively smooth surface such as CNT and MLG are less affected by mass transfer issue when catalyzing CBOR. Therefore, the PPD of direct carbohydrazide fuel cell with CNT and MLG anode catalysts is proportional to the BET surface area of such carbon materials, which is the case for porous carbon such as CB. Due to the active lone pairs of electrons on nitrogen atoms of carbohydrazide molecule, carbon atoms are proposed to be active sites for CBOR, which is also evidenced by the close single cell performance before and after the acid purification of catalysts.

The preliminary confirmation of CNT powered direct carbohydrazide fuel cell provides an optional future form of fuel cells. Future work should focus on the efficiency and durability of the fuel cell from an application point of view, and on the reaction mechanism from a scientific one.

3.2.7 References


4.1 Electrocatalytic Selective Oxidation of Glycerol to Tartronate on Au/Canode Catalysts in Anion Exchange Membrane Fuel Cells with Electricity Cogeneration

4.1.1 Graphical abstract

Figure 4.1 Graphical abstract of section 4.1.

This section is adapted from a published paper (Ji Qi, Le Xin, David J. Chadderdon, Yang Qiu, Yibo Jiang, Neeva Benipal, Changhai Liang, Wenzhen Li, Electrocatalytic selective oxidation of glycerol to tartronate on Au/C anode catalysts in anion exchange membrane fuel cells with electricity cogeneration, Appl. Catal., B 154–155 (2014) 360-368). In the past, fuel cell anode potential window is very narrow. Therefore, high selectivity of tartronate can only be obtained by consuming electricity in electrolysis cell which has a relatively large anode potential window This research lowers down the anode potential in the fuel cell and thus prevent overoxidation of tartronate to mesoxalate and C-C bond cleavage on Au/CNT catalyst, which establish a basis for designing bi-metallic catalysts.
4.1.2 Abstract

Sustainable cogeneration of tartronate (high yield of 61.8%) and electrical energy (1524 J, 12 hr) has been achieved from direct electrocatalytic oxidation of glycerol on Au/C in a 5 cm² anion exchange membrane-direct glycerol fuel cells (AEM-DGFCs). The electrode structure and reaction conditions exhibited strong effects on the anode potential, which can be tuned to <0.45 V in favour of oxidizing two primary -OH groups of glycerol while minimizing over-oxidation of the secondary –OH and C-C bond cleavage, thereby promoting the tartronate production. The relatively low activity of partial oxidation products (glycerate, tartronate, mesoxalate) on Au/C revealed in half cell indicates that the tartronate generation in AEM-DGFCs is through direct adsorbed C₃ intermediates oxidation. Mass transport of reactants and reaction intermediates governed by the operational conditions was also found to play a critical role in regulating reaction rate and the desired products selectivity. Furthermore, Au/C prepared via aqueous phase reduction method (Au/C-AQ) was compared with organic phase nanocapsule method (Au/C-NC), and it shows the residual surfactants have little effect on the tartronate yield.

4.1.3 Introduction

Non-renewable petroleum nowadays remains the main source for manufacturing of fuels and chemicals in industries, and has been serving for boosting our fast human society growth for decades. However, with the rapid increasing of the global population and continuing improvement of the people’s living standards, our heavy addiction to petroleum has aroused great concerns, mainly due to the dwindling of petroleum reserves resulting in the rising cost of the transportation fuels, and more importantly, the air quality deterioration and global
climate change.[1, 2] Under such situation, it is imperative to search for alternative, renewable natural resources for the fine chemicals production. Glycerol is a key biomass-derived compound, readily available from the bio-diesel manufacture.[3] Due to its three hydroxyl (-OH) groups, glycerol has been recognized as a viable feedstock for the production of a wide range of value-added chemicals.[4] Among them, tartronic acid (TA, a C₃ diacarboxylic acid, product of two primary -OH oxidation of glycerol) has found its medical application in the treatment of osteoporosis and obesity. However, the current high price of TA ($1536 g⁻¹) impedes the expansion of its potential market.[5]

Aqueous phase selective oxidation of glycerol to valuable chemicals (including TA) over metal catalysts with molecular oxygen or H₂O₂ oxidant represents a very attractive green process due to its low environmental impact, especially when compared to current stoichiometric oxidation processes. Although great progress has been made on selective oxidation of one primary -OH group of glycerol to glycerate over Pt, Pd, Au catalysts, it is still challenging to selectively oxidize two primary -OH groups to generate tartronate on monometallic catalysts. Prior studies were primary focused on enhancing the activity and selectivity to glycerate of Pt, Pd and Au-based mono-[6-13] and bi- metallic[10, 11, 14-16] catalysts, however under certain reaction conditions, the selectivity to di-carboxylic acid (e.g. tartronate) via consecutive oxidation of glycerol was found to be promoted. Prati and Hutchings groups have demonstrated that increasing the catalyst amount and decreasing the glycerol concentration can promote the tartronate formation, which could be attributed to the increasing of the ratio of glycerol to catalyst active sites.[7, 16, 17] It was also observed that by increasing the reaction temperature and oxygen concentration, the transformation of glycerate to tartronate could be facilitated.[7, 8] Independent studies by Prati and Davis have
reported that glycerol oxidation carried out in a fixed bed continuous up-flow reactor significantly increased the selectivity to tartronate compared with that conducted in semi-batch reactor.[18, 19] Even though research breakthrough has been made to obtain reasonable yield of tartronate, complicate multi-metallic catalysts (0.8%Ce-1.5%Bi-0.75%Pt-3%Pd/C[20] and 0.1% Bi@AuPd/AC[21]) have to be used. More importantly, conventional heterogeneous catalytic oxidation of glycerol that takes place in aqueous phase with O₂ or H₂O₂ oxidant cannot take advantage of the rich energy stored in the chemical bonds of glycerol, which can be directly converted to electrical energy via electrochemical oxidation.

Exhaustive research efforts in electrochemical oxidation of glycerol have been made aiming to gain fundamental understanding of the key factors that govern the electrocatalytic oxidations. In situ Fourier transform infrared (FTIR) spectroscopy and high performance liquid chromatograph (HPLC) combined with voltammetry have been applied to probe reaction intermediates/products under a wide range of potentials in half cells.[22-29] HPLC has identified that glycerate and glycolate are two dominant products on monometallic Pt, Pd and Au in alkaline electrolyte. Tartronate was observed as a small amount side product only on Au/C and both polycrystalline bulk Pt electrode and Pt/C at low potentials, whereas on polycrystalline bulk Au electrode, the presence of tartronate was detected as a weak FTIR signal at very high potentials of > 1.2 V vs. RHE (reversible hydrogen electrode). In addition, Simoes et al. performed the electro-oxidation of glycerol on bimetallic PdAu, PdNi, PdBi and trimetallic PdPtBi nanoparticle catalysts.[24, 30] With the assistance of spectroscopy or chromatography analysis, it was proposed that the activity of glycerol electro-oxidation could be promoted by ad-atoms and the formation of tartronate is strongly dependent on the electrode potential.
Direct glycerol fuel cells (DGFCs) have attached enormous attention as a potential mobile electrochemical power source for transportations and portable electronics. Pt-, Pd- and Au- based anode catalysts have been investigated in DGFCs with solid anion exchange membrane electrolyte.[27, 31-39] Although tremendous progress in the electrical energy generation performance have been accomplished through rational design of electrocatalyst structures, complete oxidation of glycerol to carbonate in alkaline media remains the minor reaction in comparison with its partial oxidation to various carboxylates,[40] which will lead to low energy density and utilization efficiency of glycerol fuel. For this reason, DGFCs may have industrial application potential only if reasonable output power density and high yield of higher-valued target products can be achieved simultaneously.[37, 41] Early work in our lab have successfully achieved the cogeneration of electricity (58.6 mW cm\(^{-2}\) on Pt/C and 22.7 mW cm\(^{-2}\) on Au/C) and valuable chemicals (selectivity of 41% to glycerate + 50% tartronate on Pt/C and 46% to mesoxalate on Au/C) in anion exchange membrane-direct glycerol fuel cells (AEM-DGFCs).[27, 42] Recently Vizza et al. conducted electro-oxidation of glycerol in passive AEM-DGFCs and reported selectivity of 55.3% and 43.4% to glycerate and tartronate, with electrical energy generation of 578 and 366 J on Pd-(Ni-Zn)/C and Pd/C, respectively.[33, 40] Ilie et al has reported that the fuel cell operating conditions such as anode fuel rate has an effect on the cell potential in direct glycerol fuel cell.[43] Very recently, AEM-based electrolysis flow cell reactor was self-designed by our group and used to investigate glycerol electro-oxidation on Au/C with carbon cloth substrate (liquid diffusion layer), this is similar to AEM-DGFC anode structures. It is interesting to find that the degree of glycerol oxidation can be well tuned by anode potential to produce tartronate (oxidizing two primary –OH) at < 0.45 V vs. RHE, mesoxalate (oxidizing three –OH) at ≥ 0.45 V vs. RHE, or glycolate (breaking C-
C bond) at > 0.9 V vs. RHE.[28, 44]. Therefore, it would be very attractive to seek coproduction of valuable tartronate and electricity over Au/C catalysts in AEM-DGFC, if we could lower the anode potential to <0.45V, as what we have discovered in electrolysis cell study.

Herein, we report cogeneration of electricity and tartronate with a high yield of 61.8% from direct glycerol oxidation on Au/C anode catalysts in AEM-DGFC. The optimization of membrane electrode assembly (MEA) structure, electrolyte pH, fuel flow rate and operation temperature were found to allow fine tuning of the anode potential to fairly low of <0.45 V in order to favour the electro-oxidation of two primary -OH groups of glycerol (to tartronate), while minimizing over-oxidation of the secondary -OH (to mesoxalate) and the C-C bond cleavage (e.g. to glycolate and oxalate). It is also found that in AEMFC Au/C catalyzed glycerol partial oxidation products (glycerate, tartronate, mesoxalate) are relatively stable after desorbing into bulk electrolyte, which has been further supported by half-cell experiment. For comparative purpose, Au/C anode catalysts prepared by both organic phase nanocapsule method (Au/C-NC) and aqueous phase reduction method (Au/C-AQ) were studied for electrocatalytic select oxidation of glycerol in AEM-DGFCs and it is shown that the surfactants involved in the Au/C-NC synthesis has little effect on the final oxidation products distribution.

4.1.4 Experimental section

**Chemicals**

AuCl₃ was purchased from Alfa Aesar. Sodium borohydride (99%), sodium citrate dihydrate (99%), LiBE₃H (1 M in THF), 1-octadecene (90%), and benzyl ether (99%) were purchased from Acros Organics. Carbon support (Vulcan XC72R) was obtained from Fuel
Cell Store. Polytetrafluoroethylene (PTFE), oleylamine (70%), potassium sulfate (99%), 1-propanol (99.5%) and most of the standard samples including D-glyceric acid calcium salt dehydrate (99%), sodium mesoxalate monohydrate (98%) oxalic acid (99%), glycolic acid (99%), lactic acid (90%), formic acid (98%) were bought from Sigma-Aldrich. Oleic acid (90%) and high purity glycerol (99.8%) were purchased from Fisher Scientific. All the chemicals were used as received without further purification.

**Preparation of Au/C catalysts**

Au/C prepared by organic phase nanocapsule method (Au/C-NC): AuCl₃ (151.7 mg) was dissolved in a mixture of 1-octadecene (16 mL) and oleylamine (4 mL) under a nitrogen blanket. The system was then heated to 80 °C, followed by a quick injection of LiBEt₃H (1.5 mL). After holding the temperature constant for 10 min, the solution was cooled down to room temperature and the Au nanoparticles (NPs) were separated by 10000 rpm centrifugation for 10 min. The as-prepared Au NPs were re-dispersed in hexane (50 ml) and dropped at a rate of 1 s⁻¹ into carbon black (80.6 mg or 147.7 mg) dispersed in ethanol. The as-prepared Au NPs were re-dispersed in hexane (50 ml) and slowly dropped into an ethanol dispersion of carbon black (80.6 mg or 147.7 mg). The final product Au/C-NC catalyst with a loading of 55 wt% or 40 wt% was obtained after filtration, washed with ethanol (1 L) and dried in the vacuum oven at 50 °C overnight.

Au/C prepared by aqueous phase method (Au/C-AQ): The catalyst precursor, AuCl₃ (151.7 mg), was dissolved in DI water (1500 mL) by 5 min ultrasonic sonication. The catalyst support, 80.6 mg of carbon black, was ultra-sonicated and stirred for 10 min to form a homogeneous ink. Citrate-stabilized reducing agent solution was prepared by dissolving
sodium citrate dehydrate (200 mg) and sodium borohydride (60 mg) in DI water (50 mL) and was then added to the AuCl₃ solution under vigorous stirring. Subsequently, the carbon black ink was mixed into the as-prepared Au hydrosol. In order to facilitate the deposition of Au NPs onto the carbon support, 0.4 M potassium sulfate solution (150mL) was slowly pumped into the aforementioned mixture in 12 hr. After filtrated and dried in the vacuum oven at room temperature overnight, Au/C-AQ catalyst with a loading of 55 wt% was obtained.

**Physical characterization of Au/C catalysts**

The structure, composition and morphology of Au/C catalysts were characterized by X-ray diffraction (XRD), and transmission electron microscopy (TEM). Scintag XDS-2000 θ/θ diffractometer (Cu Kα radiation (λ = 1.5406 Å) with 35 mA filament current and 45 kV tube voltage) were employed to collect XRD patterns at a continuous scan rate of 1.2 degree per minute. The mean crystallite sizes of Au/C-NC and Au/C-AQ catalysts are calculated using the (220) peak based on Debye-Scherrer formula:

\[
L = \frac{0.9 \lambda_{K\alpha}}{B_{2\theta} \cos \theta_{\text{max}}}
\]  

where L is the mean crystal size, λ is the wavelength of the x-ray (1.5406Å), B is the full width at half-maximum of the peak (rad) and θ max is the Bragg angle (rad) of Au (220).

The transmission electron microscopy (TEM) image of Au/C was collected on JEOL JEM-4000FX with an operating voltage of 200 kV.

**Membrane electrode assembly (MEA) fabrication**

The anode catalyst ink was made by mixing Au/C catalyst power, 5 wt% PTFE in water suspension into iso-propanol (10 mg catalyst/ml, mass ratio PTFE:catalyst=5:95), and sprayed
onto a carbon cloth (PTFE-untreated, 381 μm, Fuel Cell Store) that serves as the liquid diffusion layers (LDL) to achieve a loading of 1.0 mg_{Au} cm^{-2}. The cathode catalyst ink (10 mg_{catalyst}/ml, mass ratio ionomer:catalyst=3:7), which was made from 1-propanol dispersion of a commercial non-precious metal HYPERMECTM (Fe-Cu-based catalyst, Acta 4020) blended with an AS-4 anon conductive ionomer (Tokuyama), was airbrushed directly onto the AEM. Carbon paper (Toray) was employed as the cathode gas diffusion layer. The evenly-sprayed carbon cloth anode and catalyst coated membrane (CCM) cathode were dried in air under room temperature overnight before use. The MEA was fabricated by directly assembling the anode, cathode and carbon paper in sequence without hot press.

**Anion exchange membrane fuel cells (AEM-DGFCs) test and product analysis**

Electro-catalytic oxidation of glycerol in AEM-DGFC was conducted on a Scribner fuel-cell test stand (850e). The fuel cell fixture was purchased from Fuel Cell Technology Inc. with an active area of 5 cm^2. The end plate was modified with stainless steel (316L) to tolerate the alkaline operation environment. During each run, 30 ml of glycerol + KOH solution was introduced into a plastic vessel and pumped into the anode at a flow rate of 1.0 or 4.0 ml min^{-1} through a closed loop by a peristaltic pump (Gilson Minipuls 3), while the high-purity O2 (>99.999%) was fed into the cathode compartment at a flow rate of 0.1 or 0.4 L min^{-1} under a backpressure of 30 or 0 psig. The electro-oxidation was carried out by controlling the fuel cell voltage of 0.1 V. during the reaction, the anode potentials were monitored by a Hg/HgO/1.0 M KOH reference electrode and converted to reversible hydrogen electrode (RHE) by V vs. RHE = V measured vs. Hg/HgO/1.0 M KOH + 0.098+0.059×(pH of electrolyte solution). Hg/HgO/1.0 M KOH reference electrode was calibrated against RHE (HydroFlex®) in a fresh
prepared 1.0 M KOH electrolyte at the end of each test, and their potential difference was maintained 0.924 ± 0.007 V in all of the experiments. Samples were removed periodically and analyzed by HPLC using a column (Alltech, OA-1000) with a refractive index detector (RID, Agilent G1362A) and a variable wavelength detector (VWD, 220 nm, Agilent G1314A). An eluent of 5 mM aqueous sulfuric acid at a flow rate of 0.3 ml min⁻¹ were applied for the product separation. 20 µl of sample was injected into the HPLC system. Products were identified by comparison with authentic samples.

The product selectivity/yield and glycerol conversion are calculated by the following equations:

**Selectivity of one C₂ or C₃ product**

\[
\text{Selectivity of one C₂ or C₃ product} = \frac{\text{moles of C₂ or C₃ product}}{\text{total moles of C₂ and C₃ products}} \times 100\%
\]  

(2)

**Conversion of glycerol**

\[
\text{Conversion of glycerol} = \left(1 - \frac{\text{concentration of glycerol at certain time}}{\text{Initial concentration of glycerol}}\right) \times 100\%
\]  

(3)

**Yield of C₂ or C₃ product**

\[
\text{Yield of C₂ or C₃ product} = \text{selectivity of C₂ or C₃ product} \times \text{conversion of glycerol}
\]  

(4)

The carbon balance is based on[19, 45]:

**Carbon balance**

\[
\text{Carbon balance} = \frac{3M_{gi} - 3\sum M_{c₃} - 2\sum M_{c₂} - 1\sum M_{c₁} - 3\sum M_{gₙ}}{3M_{gi}} \times 100\% 
\]  

(5)

where \( M_{gi} \) and \( \sum M_{gₙ} \) is the initial and final moles of glycerol in the electrolyte. \( \sum M_{c₃}, \sum M_{c₂} \) and \( \sum M_{c₁} \) is the total moles of C₃ (glycerate, tartronate, mesoxalate, lactate), C₂ (glycolate, oxalate, glyoxylate) and C₁ (formate, carbonate) products, respectively.
If assuming that no C-C bond cleavage occurs in C₂ products, then. Thus \( \sum M_{c2} = \sum M_{c1} \), the equation for carbon balance calculation can be simplified to:

\[
\text{Carbon balance} = \frac{M_{gi} - \sum M_{c3} - \sum M_{c2} - \sum M_{g}}{M_{gi}} \times 100\%
\]  

(6)

Therefore, a carbon balance of 0 means all the C₂ products generated from C-C breaking of C₃ products do not undergo further C-C cleavage, and the summation of all the C₂ and C₃ products and unreacted glycerol is equal to the initial glycerol. A smaller carbon balance value indicates less C₂ intermediates were further oxidized to C₁ products (carbon balance of 0 means no C₂ intermediates were further oxidized to C₁ products). The carbon balance under all the tests condition is less than 15%, which is within the system error expected in HPLC analysis.

**Half cell test**

Half cell tests were performed in a conventional three-electrode-cell setup, equipped with a glassy carbon working electrode, and Hg/Hg (1.0 M KOH) reference electrode and a Pt wire counter electrode. A water bath is used to hold system temperature at 25, 50, or 60 °C throughout the tests. 2.0 mg Au/C (55 wt%) was firstly dispersed in 1.0 ml isopropanol by sonication to form uniform ink. Before each test, 20 µl of the 2.0 mg ml⁻¹ catalyst ink was then drop-casted on the glass carbon electrode, followed by adding 10 µl of 0.05 wt% AS-4 anion conductive ionomer (Tokuyama) on the top to bind the catalyst particles. Prior to tests, all the electrolytes were deacerated by purging with N₂ gas (99.99%) for 30 min. Ten cyclic voltamograms (CVs) were recorded for Au/C catalyst at 25, 50, and 60 °C in 0.1 M KOH and the stabilized polarization curve obtained from the last cycle as reported. All potentials were
reported with respect to RHE. A linear sweep voltammetry (LSV) on Au/C catalyst with a sweep rate of 1 mV s\(^{-1}\) without a rotation was carried out in 0.1 M KOH, 0.1 M KOH + 0.1 M glycerol, 0.2 M KOH + 0.1 M glycric acid, 0.3 M KOH + 0.1 M tartronic acid and 0.1 M KOH + 0.1 M sodium mesoxalate monohydrate at 50 or 60 °C. Excessive KOH (0.2 or 0.3 M) was used to neutralize glycric acid (pKa = 3.52) and tartronate (pKa1 = 2.42, pKa2 = 4.54).[46]

4.1.5 Results and discussion

The effects of MEA structures and reaction conditions on the tartronate selectivity in AEM-DGFC and electro-oxidation activity evaluation of main glycerol partial oxidation C\(_3\) products in half cell

Electrocatalytic oxidation of glycerol in AEM-DGFCs could provide a new route to sustainable conversion of glycerol to value-added oxygenated chemicals with important industrial applications. The AEM-DGFCs can be envisioned as a continuous fixed-bed reactor with multiple plates, which is more prone to produce deeply oxidized products than conventional heterogeneous catalytic oxidation of glycerol in semi-batch reactor configuration.[17-19] In electrocatalysis, the oxidation reactions take place at the electrified catalyst-electrolyte interface close to the anode, where the reaction rate, pathway and products distribution can be regulated via manipulation of the anode potential, so as to facilitate the formation of valuable target products. Considering that glycerol electro-oxidation on Au/C in AEM-DGFCs involves complex reaction sequences, any changes in reaction conditions, such as the electrode thickness, flow rate, the reaction temperature and electrolyte pH, could affect the anode potential, thereby influencing the final products distribution.
Figure 4.2 Electro-catalytic selective oxidation of glycerol in AEM-DGFCs with different MEA structures and operation conditions. Anode catalyst: Au/C-NC; Cathode catalyst: Fe-Cu-based catalyst (Acta 4020); Anode fuel: 1.0 M glycerol in KOH electrolyte, 30 ml; Glycerol:Au = 1:1300 (mol:mol); Cell voltage: 0.1 V; reaction time: 1 h. Details of MEA structure and operation conditions (a)-(e) are listed in Table 4.1.
Table 4.1 Details of MEA structure and AEM-DGFC operation conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane type&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>A901</td>
<td>A901</td>
<td>A901</td>
<td>A901</td>
</tr>
<tr>
<td>Anode catalyst loading (mg cm&lt;sup&gt;-2&lt;/sup&gt;)</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cathode catalyst loading (mg cm&lt;sup&gt;-2&lt;/sup&gt;)</td>
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<td>3</td>
<td>3</td>
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<tr>
<td>Anode catalyst metal loading (% wt)</td>
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<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Anode fuel flow rate (ml min&lt;sup&gt;-1&lt;/sup&gt;)</td>
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<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cathode gas flow rate (ml min&lt;sup&gt;-1&lt;/sup&gt;)</td>
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<td>400</td>
<td>100</td>
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<tr>
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<td>60</td>
</tr>
<tr>
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<tr>
<td>Back pressure (psi)</td>
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<td>30</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

a. The MEA structure and operation conditions were used in our previous work [16].

b. The thickness of Tokuyama A201 and A901 membrane is 28 μm and 10 μm, respectively.
Figure 4.3 Linear sweep voltammograms of Au/C-NC (55 wt%) in 0.1 M KOH + 0.1 M glycerol, 0.2 M KOH + 0.1 M glyceric acid, 0.3 M KOH + 0.1 M tartronic acid, 0.1 M KOH + 0.1 M sodium mesoxalate salt and 0.1 M KOH at a scan rate of 1 mV s\(^{-1}\), without rotation, (a) 50 °C, (b) 60 °C.
Electrode thickness was first optimized towards anode potential tuning for selective oxidation of glycerol in AEM-DGFC. The different anode thicknesses (length scales) result in different time scales of which the reactants diffuse into and products diffuse out of the porous electrodes, which affect the concentration profiles of reactants and reaction intermediates available inside the electrocatalytically active region. In other words, the thicker the porous electrode is, the more reaction intermediates will be held within the confined electrolyte volume to possibly facilitate their deeper oxidation, meanwhile, the fresh reactant will be held outside of the electrocatalytically active region. Increasing the metal loading of Au/C catalyst from 40 wt% to 55 wt% decreases the amount of carbon black amount on the anode (from 7.5 mg to 4.0 mg), therefore decreases the thickness of the porous liquid diffusion anode (from 705 µm to 597 µm, including the thickness of carbon cloth substrate of 381 µm and catalyst layer of 324 µm or 216 µm measured by a micrometer), given that the same Au loading (1.0 mg$_{\text{Au}}$ cm$^{-2}$) was used at the anode. Compared to the Au/C (1.0 mg$_{\text{Au}}$ cm$^{-2}$, 40 wt%) anode used in our previous work,[42] the presented thinner porous anode structure (1.0 mg$_{\text{Au}}$ cm$^{-2}$, 55 wt%), allows more fresh glycerol from bulk electrolyte to replenish the oxidation reaction, which leads to the glycerol conversion increasing from 13.1% (Figure 4.1(a)) to 14.7% (Figure 4.1(b) in 1 hour operation. Higher local concentration of glycerol presented at the catalyst-electrolyte interface will not only negatively shift the onset potential of glycerol electro-oxidation in half cell but also increase the open circuit voltage (OCV) in AEM-DGFC, as it facilitates the formation of highly reactive glyceraldehyde.[38, 47] The cathode non-precious Fe-Cu-based catalyst loading was also increased from 1.0 mg/cm$^2$ to 3.0 mg/cm$^2$ to facilitate oxygen reduction reaction (ORR). It was observed that the measured anode potential decreases from 0.54 V to 0.41 V vs. RHE with the anode thickness decreasing and enhanced ORR. This
observation can also be explained by the ease of the removal of reaction intermediates by glycerol fluxing in through the thinner porous electrode, as their presence could inhibit the oxidation of glycerol[48] and lead to the anode potential increasing. The independent linear scan voltammetry (LSV) experiments were carried out at 50 °C by using KOH solution with glycerate, tartronate, or mesoxalate.(Figure 4.2 (a)) It shows that glycerate is more difficult to be oxidized on Au/C than glycerol as shown by its lower peak current density (e.g. 4.5 mA cm\(^{-2}\) vs. 23.6 mA cm\(^{-2}\) at 50 °C) and more positive onset potential (e.g. 0.82 V vs. ca. 0.57 V (vs. RHE) at 50 °C). It needs even higher onset potentials of about 1.2 and 1.3 V vs. RHE, respectively, for tartronate and mesoxalate adsorption and oxidation on Au/C. This strongly indicates that desorbed glycerate, tartronate and mesoxalate are difficult to be further oxidized under the fuel cell operation conditions (low anode potentials).

As already noted in the previous publications, the C-C cleavage product glycolate is nearly inert on both Au smooth polycrystalline and nanoparticle electrodes.[49, 50] Therefore, lowering anode potential and enhancing mass transport using the modified thin electrode structure can promote the tartronate formation by the sequential oxidation of glycerol via adsorbed C\(_3\) reactive intermediates, while minimize its over-oxidation to mesoxalate or C-C bond cleavage by-products (glycolate and oxalate), leading to the tartronate selectivity increasing from 34% (Figure 4.1(a)) to 49% (Figure 4.1(b)) in 1 hour. However, the decreasing of the anode potential weakens the adsorption of glyceraldehyde, a possible unstable byproduct generated at low potential (0.4 V vs. RHE).[26] The desorbed glyceraldehyde decomposes in the bulk alkaline electrolyte, which is likely responsible for the lactate detected in the final products profile (Figure 4.1(b)).[51]
Glycerol fuel flow rate for the AEM-DGFC reactor was also optimized to study its effect on the reaction rate and product distribution of glycerol electro-oxidation. Under similar reaction conditions, the liquid flow rate was decreased from 4 ml min\(^{-1}\) to 1 ml min\(^{-1}\) and the results are shown in Figure 4.1 (b) and (c). After slowing down the flow rate of 2.0 M KOH + 1.0 M glycerol, it is observed that the glycerol conversion drops from 14.7% to 11.5%, which could also be attributed to the more intimate contact between the reaction intermediates and catalyst confined within the porous electrode through lowering the fuel flow rate. Although the fuel flow rate has a minor effect on the anode potential, the increasing of the retention time can help hold/trap the reaction intermediates within the porous matrix of the anode, therefore, glyceraldehyde is more likely to remain chemisorbed at the surface and undergoes consequential oxidation to mesoxalate. This is evidenced by the mesoxalate selectivity increasing from 10% to 13% and the selectivity of the glyceraldehyde-degraded byproduct lactate decreasing from 6.0% to 2.6%.

In order to gain insight into the influence of reaction temperature on electro-oxidation of glycerol, CV was performed on Au/C (55 wt%) catalyst in blank 0.1 M KOH at 25, 50, and 60 °C. It is shown in Figure 4.3 that with the temperature increasing, the onset potential where Au starts to adsorb OH shifts negatively, and within the potential window investigated (< 1.65 V vs. RHE), the oxygen evolution reaction (OER) activity on Au/C is negligible at 25, 50, and 60 °C. Early studies suggested that the presence of the sub-monolayer of the adsorbed OH governs the catalytic behaviour of Au for alcohol oxidation,[49] and there is no glycerol adsorption before the onset potential of Au(OH) formation.[52] Recent DFT results also
indicated that the adsorbed OH will significantly lower the activation barrier for both O-H and C-H bond dissociation and enhance the catalytic activity of Au\cite{45}:

\begin{align}
H_\beta R - O H_\alpha + O H_{ads} \rightleftharpoons H_\beta R - O_{ads} + H_2O \\
H_\beta R - O H_\alpha + O H_{ads} \rightleftharpoons R = O_{ads} + H_2O
\end{align}

Figure 4.4 Cyclic voltammograms of Au/C-NC (55 wt\%) in 0.1 M KOH at 25, 50, or 60 °C, at a scan rate of 50 mV s\(^{-1}\), without rotation.

In our previous studies, it is shown that the onset potential of the glycerol electro-oxidation on Au/C in half cell shifts negatively, as the reaction temperature increases from 25 °C to 60 °C, which could be attributed to the higher adsorption rate of OH on Au at elevated temperatures\cite{47}. In addition, the reported voltammograms also indicated better electro-
oxidation kinetics was achieved at higher temperatures, as shown by the increasing of the peak current density. In agreement with these prior results, it is observed that the AEM-DGFCs operated at higher temperature (60 °C) promotes the glycerol conversion from 11.5% (Figure 4.1(c), 50 °C) to 13.5% (Figure 4.1(d), 60 °C) in 1 hour. Moreover, it further decreases the anode potential from 0.40 V to 0.35 V vs. RHE, contributing to the increasing of tartronate selectivity to 54.8%. On the other hand, the elevated reaction temperature may also promote the reaction intermediates diffusion to the bulk electrolyte, which prevents the further oxidation to mesoxalate, leading to mesoxalate selectivity drop from 13.0% to 9.4%. The byproduct lactate selectivity remains small (2.3%), mainly due to the rapid oxidation of glycerol to glyceraldehyde at the higher temperature.

High pH alkaline environment has been reported to effectively improve glycerol electro-oxidation rate.[27, 38, 44, 53, 54] The AEM-DGFCs fed with 8.0 M KOH + 1.0 M glycerol shows appreciably increasing of the tartronate selectivity from 54.8% to 70.6% and the glycerol conversion from 13.5% to 18.2% when compared to 2.0 M KOH + 1.0 M glycerol (Figure 4.1(e)). Higher OH⁻ concentration was reported to benefit the initial base-catalyzed dehydrogenation of alcohol to promote the generation of highly reactive alkoxy intermediate by lowering the activation barrier[51]:

$$H_\beta R - OH_\alpha + OH^- \leftrightarrow H_\beta R - O^- + H_2O \leftrightarrow H_\beta R - O_{ads} + e^-$$

(9)

On the other hand, higher OH⁻ concentration in the bulk electrolyte will increase OH_{ads} coverage rate on Au surface. As aforementioned, the OH_{ads} will also facilitate the elimination of both H_\alpha and H_\beta of adsorbed alcohols through the metal surface catalyzed process (equation 7 and 8). As a result, the electrolyte with higher pH (8.0 M KOH + 1.0 M glycerol) greatly enhances the reaction rate, giving rise to the observed higher glycerol conversion and lower
anode potential (0.29 V vs. RHE). This result can be supported by our previous studies of
electro-oxidation of glycerol over Au/C in half cell, which showed that the onset potential of
glycerol oxidation shifted negatively with the KOH concentration increasing.[38] The very
low anode potential favours the tartronate formation with a selectivity of 70.6% determined by
HPLC analysis. A slight increase of lactate could be also attributed to this low anode potential
achieved, as it weakens the adsorption of glyceraldehyde on the Au catalyst. Additionally, the
increment of OH$_{\text{ads}}$ on Au surface promotes the removal of adsorbed C$_3$ intermediate
species[24, 53] to form glycerate or tartronate, before they undergo further oxidation to
mesoxalate or C-C bond breaking to byproducts of glycolic and oxalate.

Tartronate has a significant market potential. A very high tartronate selectivity of 70.6
% from direct glycerol electro-oxidation has been achieved in the AEM-DGFC reactor through
fine tuning of anode potential, which was achieved by the optimization of the electrode
structure and reaction conditions. It is worthy to note that the optimization of mass transfer of
the reactant, intermediates and products by varying these operation conditions also plays a
critical role in regulating the reaction rate and pathway to the desired products.

**Cogeneration of electricity and tartronate with high yield in AEM-DGFC**

Compared with the traditional heterogeneous catalysis, electrocatalytic selective
oxidation of glycerol in the AEM-DGFC reactor is a more sustainable process, in which the
valuable chemicals and electrical energy can be simultaneously generated.[27, 42] As
tartronate finds its values in the pharmaceuticals[55] food industries[56-58] and anti-corrosive
protective agents[59], we focused our efforts on employing the optimum conditions, as listed
in Table 4.1(e) demonstrating the highest activity and selectivity to tartronate, so as to achieve
the high yield of tartronate for potential industrial synthesis applications.
Figure 4.5 Electro-catalytic selective oxidation of glycerol on Au/C-NC (55 wt%) in AEM-DGFC under optimized condition for high yield of tartronate. Anode catalyst: Au/C-NC (1 mgAu cm⁻²); Cathode catalyst: Fe-Cu-based catalyst (Acta 4020, 3 mg cm⁻²), anion exchange membrane (A901, Tokuyama Inc.). Anode fuel: 8.0 M KOH + 1.0 M glycerol, 30 ml, 1.0 ml min⁻¹; Cathode fuel: high purity O₂, 100 ml min⁻¹, ambient pressure. Glycerol:Au = 1:1300 (mol:mol); Cell voltage: 0.1 V; Cell temperature: 60 °C reaction time: 12h.

The reaction profile shown in Figure 4.4 exhibits that electrocatalytic selective oxidation of glycerol can achieve a tartronate yield of 61.8% (69.3% of selectivity at 89.2% glycerol conversion) after 12 h, concurrently with energy release of 1534 J in the AEM-DGFC reactor with Au/C-NC under the optimized conditions. The maximum yields of tartronate from
heterogeneous catalytic oxidation of glycerol have been reported to be 58% on Ce-Bi-Pd-Pt/C[20] and 78% on Bi@AuPd/C[21]. However, mono-Au or AuPd, AuPt heterogeneous catalysts were found to be rather inefficient for tartronate production from direct glycerol oxidation.[5] The high tartronate yield on Au/C electrocatalyst achieved in this work may open an alternative route to sustainable electrocatalytic conversion of biorenewable intermediates to chemicals along with electricity cogeneration.

Figure 4.4 also shows that as the reaction was prolonged to 12 h, the glycerol conversion reached 89.2% and the tartronate selectivity only slightly decreased from 70.6% to 69.3%, even though the anode potential of the AEM-DGFC kept increasing from 0.29 V to 0.48 V vs. RHE. This indicates that the final products distribution in bulk electrolyte is governed by both the electrocatalytic reaction at the electrified catalyst-electrolyte interface that can be regulated by the anode potential, and the reactants/reaction intermediates/products diffusion/transport through the catalyst layer. As discussed previously, the MEA structure and reaction conditions of AEM-DGFC were optimized to not only lower the anode potential so as to favour the consecutive oxidation of glycerol to tartronate with less C-C bond cleavage or over-oxidation to mesoxalate, but also facilitate desorption of the intermediates/products off the catalytic active sites and diffusion back to the bulk electrolyte.

The LSVs performed on Au/C-NC in half cell at 60 °C with alkaline electrolytes of glycerate, tartronate, mesoxalate and glycerol are shown in Figure 4.2(b). The results showed the electrocatalytic activity sequence of these desorbed glycerate, tartronate and mesoxalate during the glycerol electro-oxidation. Higher anode potentials are needed to make them reactive on Au/C-NC electrode. In addition, previous studies by Lamy et al. have found that the glycolate and oxalate cannot be oxidized on Au electrode in alkaline solution in the
potential range of 0 V – 1.0 V vs. RHE, which is within the fuel cell anode potential window.[49] For this reason, the products presented in the bulk electrolyte are more difficult to re-adsorb and further oxidize on the Au catalyst as compared with glycerol, resulting in the relatively stable products distribution in the bulk electrolyte and no apparent change in the product selectivity from 1 hour to 12 hours. In particular, the relatively low activity (onset potential and peak current density) of electro-oxidation “desorbed” tartronate may account for its high selectivity.

However, as glycerol was continuously converted, increasing concentrations of glycerate and tartronate will accumulate in the product mixture solution. It is reported that the adsorption of glycerate or tartronate during the glycerol oxidation could strongly deactivate metal catalysts in the heterogeneous catalysis system, which is attributed to the formation of ketonic species.[48, 60]. To investigate the influence of the product salts on the rate of glycerol electro-oxidation, equal molar glyceric acid was added to a 0.1 M glycerol solution. Additional KOH was also added to neutralize the glyceric acid in order to maintain a close base to reactant ratio of around 1:1 (mol:mol). Chronoamperometries (CAs) were carried out on Au/C-NC at 0.8 V vs. RHE, where the electro-oxidation proceeds slowly so that the mass transport effect is negligible. Figure 4.5(a) shows that the oxidation current density of 0.1 M glycerol remains at ca.0.28 mA cm\(^{-2}\) after 1800 s test, while with addition of 0.1 M glycerate, it is significantly lower and drops rapidly to 0.014 mA cm\(^{-2}\). The controlled CA experiment using 0.2 M KOH
Figure 4.6 (a) Influence of glycerate on the chronoamperometric activity of glycerol oxidation on Au/C-NC (55 wt%) at 0.8 V vs. RHE, 25 °C; (b) Cyclic voltamograms of Au/C-NC (55 wt%) before and after chronoamperometry (CA) tests with the addition of glyceric acid, used Au/C-NC catalyst was washed with deionized water before the recycle test, 1.0 M KOH, 25 °C

+ 0.1 M glyceric acid showed no current generation on Au/C-NC under the same test conditions, which suggests that the decreased reaction rate is not due to the competitive electro-oxidation of glycerate, but rather due to the inhibitory effect of glycerate. It is worth to mention
that the adsorbed glycerate could be washed off with copious deionized water and the active sites of Au/C-NC can be recovered, as evidenced by the similar broad peaks correlated to the reduction of AuOx during the cyclic voltammetry in 1.0 M KOH before and after CV tests (Figure 4.5b). The mechanism of the inhibition of supported metal catalysts by reaction intermediates/products formed in the course of the electro-oxidation of glycerol is still elusive and currently under study in our lab. Nevertheless, the deactivation of Au/C-NC will cause the activity loss of the glycerol electro-oxidation and is responsible for the increasing of the anode potential in AEM-DGFC with the elongated reaction time, as shown in Figure 4.4. As a result of anode potential increasing, the selectivities to C-C cleavage products glycolate and oxalate, were increased from 0.8 % (after 1 h) to 1.2 % (after 12 h) and 2.5 % (after 1 h) to 3.8 % (after 12 h), respectively.

The effect of supported gold nanoparticle synthesis method on glycerol selective electro-oxidation

The essential role of metal catalysts well recognized in both electrocatalysis and heterogeneous catalysis is to enhance the adsorption, activation and transformation of reactants and reaction/reactive intermediates. Various synthesis routes have been provided to prepare metal catalysts with controlled size, size distribution, structure and morphology, which can drastically affect the activity and selectivity of the heterogeneous catalysts.[8, 10-12, 15, 61] Aiming to study the effect of metal nanoparticle catalyst synthesis methods on the electrocatalytic oxidation of glycerol, we compared electrocatalytic oxidation of glycerol over
Figure 4.7 TEM images and particle size histograms of (a) Au/C-NC, (b) Au/C-AQ; and (c) XRD patterns of Au/C-NC and Au/C-AQ (55 wt% Au loading)

Au/C catalysts prepared via two synthesis methods, namely nanocapsule method (Au/C-NC) and aqueous-phase reduction method (Au/C-AQ). The Au/C-NC was prepared by reduction of
AuCl₃ precursor in organic phase solution and C₁₈ surfactant oleylamine served as the stabilizer; while the Au/C-AQ was prepared by reduction of AuCl₃ in water phase and citrate was used as the stabilizer. TEM images show that the average particle size of Au/C-NC is 3.0 nm (Figure 4.6(a)), which is smaller than that of 4.7 nm for Au/C-AQ (Figure 4.6(b)). The crystal sizes obtained from (220) diffraction peaks of XRD are 2.1 nm and 4.6 nm for Au/C-NC and Au/C-AQ, respectively, which agrees well with the TEM characterizations. It is important to note that the size distribution of Au/C-NC ranging from 1-6 nm is also narrower than that of 1-10 nm for Au/C-AQ. The variation of particle sizes and size distributions observed from the two preparation methods can be attributed to the nature of stabilizers and solvent used. Oleylamine with a long-chain primary alkyl-amine can act as electron donor and has strong affinity to Au nanoparticles at the synthesis temperature (80 °C),[62] whereas citrate is purely an electrostatic stabilizer that interacts weakly with the Au nanoparticles.[61] Therefore, the organic phase based nanocapsule method can protect Au particles more effectively from aggregation in the preparation process compared to aqueous phased based method.
Figure 4.8 Electro-catalytic selective oxidation of glycerol on Au/C-AQ (55 wt%) in AEM-DGFC under optimized condition for high yield of tartronate. Anode catalyst: Au/C-AQ (1 mgAu cm\(^{-2}\)); Cathode catalyst: Fe-Cu-based catalyst (Acta 4020, 3 mg cm\(^{-2}\)), anion exchange membrane (A901, Tokuyama Inc.). Anode fuel: 8.0 M KOH + 1.0 M glycerol, 30 ml, 1.0 ml min\(^{-1}\); Cathode fuel: high purity O\(_2\), 100 ml min\(^{-1}\), ambient pressure. Glycerol:Au = 1:1300 (mol:mol); Cell voltage: 0.1 V; Cell temperature: 60 ºC reaction time: 12h.

The electro-catalytic oxidation of glycerol over Au/C-AQ anode catalyst was performed in AEM-DGFC under the same optimal conditions as Au/C-NC. Figure 4.7 shows that glycerol conversion of 95.6% was achieved on Au/C-AQ together with energy generation
of 1666 J, which are higher than those for Au/C-NC (89.2% with 1534 J of energy generation, Figure 4.4). However, the tartronate yield on Au/C-AQ was 61.2% with 10.5 % carbon balance, which is very close to 61.8% with 12.5 % carbon balance on Au/C-NC as shown in Figure 4.4. A possible explanation of different activities may lie in the residual hydrophobic oleylamine on the Au surface[63] limits the accessibility of fresh glycerol across the surfactant ligand layers. The relatively clean surface of Au/C-AQ realized by easy removal of citrate also increases the residence time of reactants / reaction intermediates near the Au/C-AQ active sites and liberates a fraction of active sites for the sequential glycerol electro-oxidation, thus enhancing the rate of further oxidization of the secondary -OH of adsorbed C₃ species to mesoxalate or C-C breakage of adsorbed C₃ species to glycolate and oxalate, following the pathway proposed in our previous publications.[28, 42, 44] As a result, after the 12 hours reaction, the selectivities to mesoxalate from 8.9% to 2.8%, glycolate from 3.0% to 2.1%, oxalate from 8.6% to 9.6% on Au/C-AQ were observed, which are higher than 4.3% to 1.2% (mesoxalate), 0.8% to 1.2% (glycolate) and 2.5% to 3.8% (oxalate) on Au/C-NC. The changed product selectivity during the reaction is perhaps due to the change of Au polarization (anode potential), resulting from the continuous conversion of glycerol and change in product distribution. Furthermore, our results are in good agreement with Hutching’s group work [64]: the surfactant bonded to catalyst surface will not apparently change the product yield, while a clean catalyst surface could enhance the reaction rate. Research on preparation of Au-based bimetallic catalysts for electro-oxidation of glycerol in AEMFC is currently underway in our lab.
4.1.6 Conclusions

Electrocatalytic selective oxidation of glycerol over Au nanoparticle catalysts to tartronate with a high yield of 61.8% with cogeneration of electrical energy of 1524 J (12 hrs) has been achieved in a 5 cm$^2$ AEM-DGFCs. The MEA structure and reaction conditions were found to be able to strongly influence tartronate selectivity during the glycerol electro-oxidation. Rational optimization of the MEA structure, flow rate, oxidation temperature as well as the electrolyte pH could not only tune the anode potentials to <0.45 V in favour of tartronate production, but also improve the mass transport of the reactant and products / intermediates so as to improve the reaction kinetics and desorption rate of produced tartronate off the active sites. The half-cell study on electro-oxidation of C$_3$ products (glycerate, tartronate and mesoxalate) shows they are less active than glycerol on Au/C, therefore, they are not likely to be further oxidized upon diffusion into the bulk electrolyte. Particularly, the lowest electro-oxidation activity of tartronate may be related with its high selectivity and yield. Furthermore, two Au/C catalysts prepared through the nanocapsule method (Au/C-NC) and aqueous-phase reduction method (Au/C-AQ) were investigated for the electro-catalytic oxidation of glycerol. Au/C-AQ has larger particle size (4.7 nm vs. 3.0 nm for Au/C-NC) and broader size distribution (1-10 nm vs. 1-6 nm for Au/C-NC) due to the different nature of capping agents employed in the synthesis. Under the same electro-oxidation reaction conditions, the conversion of glycerol obtained on Au/C-AQ with cleaner surface was 95.6% in 12 h, which was higher than Au/C-NC of 89.2%, resulting in higher electrical energy generation (1666J vs. 1524J). However, the residual surfactants presented on Au/C-NC do not apparently change the product yield, evidenced by the very close tartronate yields with Au/C-AQ (61.2%) and Au/C-NC (61.8%).
4.1.7 References


4.2 Electro catalytic Selective Oxidation of Glycerol to Tartronate and Electricity Generation
Using Au, Pd Mono and Bimetallic Nanoparticles Supported On Carbon Nanotube As Anode Catalyst in Anion Exchange Membrane Fuel Cell

This section is unpublished work. This research designs bimetallic PdAu/CNT catalyst by combining different active sites (Pd and Au) which have different functions so that the reaction rate and target product yield can be improved simultaneously. For electrocatalytic oxidation of glycerol, it is found Pd can re-adsorb the desorbed glycerate in bulk electrolyte and further oxidize it to tartronate while Au can protect C-C bond of C$_3$ species. Therefore, combining Pd and Au takes advantage of these effects synergistically, maximizing the yield of tartronate in electrocatalytic glycerol oxidation reaction. This work provides new insights into the synergistic effects of bimetallic PdAu catalysts for selective oxidation of glycerol.

4.2.1 Abstract

As a renewable biomass feedstock, glycerol can be valorized to a series of chemical products, among which tartronic acid is one of the most expensive chemicals. Since glycerol oxidation reaction (GOR) is a spontaneous reaction with negative Gibbs free energy change, it’s suitable to investigate GOR in a fuel cell to simultaneously obtain a high yield of value-added product and high electricity output. Studying the GOR in fuel cell not only has profitable application value, but also provides new scientific insights into the difference between electrocatalytic reaction process and heterogeneous catalytic reaction process.

In the present work, Au, Pd mono and bimetallic nanoparticles supported on carbon nanotube (CNT) were prepared and used for glycerol oxidation in anion exchange membrane fuel cell. For electrocatalytic oxidation of glycerol, it is found Pd can re-adsorb the desorbed
glycerate in bulk electrolyte and further oxidize it to tartronate while Au can alleviate C-C bond cleavage of C3 species. Therefore, combining Pd and Au takes advantage of these effects synergistically, maximizing the yield of tartronate in electrocatalytic glycerol oxidation reaction. Alloyed PdAu also increases glycerol and glycerate reaction rate so that higher power output and shorter reaction time can be achieved. During the 8 h reaction process, stable 50 mW cm\(^{-2}\) to 5 mW cm\(^{-2}\) can be generated with 68.4 % yield of tartronate finally achieved using PdAu alloyed nanoparticles supported on CNT as an anode catalyst.

4.2.2 Introduction

With the gradual depleting of fossil fuels, it is inevitable to replace the petroleum-based refinery to biomass-based refinery for a sustainable future. As an important biomass derived feedstock, glycerol is facing a price downward as a result of the massive increase of biodiesel production worldwide.[1] New outlets of glycerol such as valorisation of it to other chemicals is creating more profitable chances. [2] One of the most expensive glycerol derived compound (1564 US$/g), tartronic acid (TA), is applied as bones dysmetabolism medicine [3] and anti-corrosive protective agent [4]. To make these applications more practical and further develop other functions, the price of TA has to be lowered down by increasing the selectivity and yield of it from glycerol oxidation reaction (GOR).

With 0.8%Ce-1.5%Bi-0.75%Pt-3%Pd/C catalyst, Kimura et al. reported 58 % yield of sodium tartronate for GOR performed in basic media [5], which demonstrated the selective oxidation of 2 primary hydroxyl groups in the glycerol molecule using standard heterogeneous catalysis process. In this catalyst composed of 4 metals, bismuth and ceria work as promoters for platinum and palladium to facilitate the further oxidation of glycerate and activate the
glycerol, respectively.[2] Gallezot et al. confirmed that bismuth is promoting the consecutive oxidation of glyceric acid to tartronic acid.[6] Taking advantage such consecutive oxidation, Prati et al further increased the tartronate yield to 78 % by modifying PdAu alloy with Bi. [7]

Since GOR is oxidation reaction with negative Gibbs free energy change, it can be used as anode reaction in fuel cell to generate electricity from the energy stored in its chemical bonds while producing chemicals. We previously investigated electrocatalytic GOR on Au/C catalyst[8, 9] in fuel cell to simultaneously obtain 61.8 % yield of potassium tartronate and 1524 J electricity output by lowering down the anode potential. [9] It is found that at 60 °C within the fuel cell anode potential (<0.7 V vs RHE) desorbed tartronate in the bulk electrolyte is relatively stable on Au catalyst without obvious consecutive oxidation, which makes tartronate an ideal end product. However, desorbed glycerate is more difficult to be re-adsorbed and consecutively oxidized on the Au catalyst, which prevents the yield of tartronate from further increasing. Similar phenomena (100 % selectivity to glycerate) has also been observed in the non-electrocatalytic heterogeneous oxidation of glycerol by Hutchings et al.[10] Therefore, with the help of other elements as to promote consecutive oxidation of reaction intermediates, more selective catalyst can be designed.

Pd-based catalyst has been proved to be highly active and stable for direct alcohol fuel cells (DAFCs).[11] Although not active as Pt, Pd is more abundant and cheaper than Pt,[12] and is suitable for electrochemically catalyzing alcohol oxidation in alkaline media. Furthermore, PdAu bimetallic catalyst has been reported to have higher selectivity to tartronate than Au monometallic catalyst in the non-electrocatalytic heterogeneous oxidation of glycerol[13], making Pd a suitable candidate as a second element to improve the yield of tartronate.
In this work, electrocatalytic selective oxidation of glycerol over bimetallic PdAu supported on CNT (PdAu/CNT) yielded 68.4% of potassium tartronate (fuel:catalyst molar ratio is 1000) in 5 cm² AEM-DAFC, which is higher than that over Au/CNT (41.0%) and Pd/CNT (62.0%). Three major synergetic effects of palladium and gold have been discovered to maximize tartronate yield. Firstly, desorbed glycerate can be re-adsorbed and consecutively oxidized on Pd but not on Au in fuel cell anode potential range (< 0.7 V vs. RHE). The sequential oxidation of the second primary hydroxyl group on Pd helps the bimetallic catalyst to minimize the unwanted glycerate yield as a reaction intermediate. Secondly, Au helps the bimetallic catalyst to protect the C-C bond of C₃ species, alleviating the GOR from producing high yield of C₂ oxalate. Thirdly, the reaction rate on the bimetallic PdAu/CNT is faster than that on Au/CNT and Pd/CNT, leading to a higher energy output and glycerol conversion in unit time.

4.2.3 Experimental section

Chemicals

The short multi-walled CNT (10-20 nm outer diameter, 0.5-2 μm length) was purchased from Cheaptubes Inc. Carbon support (Vulcan XC72R) was obtained from Fuel Cell Store. K₂PdCl₄ (98%), AuCl₃ (99%), polytetrafluoroethylene (PTFE), oleylamine (70%), potassium sulfate (99%), 1-propanol (99.5%) and most of the standard samples including D-glyceric acid calcium salt dehydrate (99%), sodium mesoxalate monohydrate (98%) oxalic acid (99%), glycolic acid (99%), lactic acid (90%), formic acid (98%) were bought from Sigma-Aldrich. Oleic acid (90%) and high purity glycerol (99.8%) were purchased from Fisher Scientific. The catalyst 4020 was ordered from Acta, Inc. Sodium borohydride (99%) and sodium citrate
dihydrate (99%) were manufactured by Acros Organics. All the chemicals were used as received without further purification.

**Preparation of Au/CNT, Pd/CNT and PdAu/CNT catalysts**

Au/CNT, Pd/CNT and PdAu/CNT (20 % total metal weight percentage) are prepared by aqueous phase method. A typical procedure of preparing PdAu/CNT is provided as follows. Pd/CNT and Au/CNT are prepared with similar procedures. The catalyst precursor, AuCl₃ (41.5 mg) and K₂PdCl₄ (44.6 mg) was dissolved in DI water (1500 mL) by 5 min ultrasonic sonication. The catalyst support, 157.8 mg of carbon nanotube (CNT), was ultra-sonicated and stirred for 10 min to form a homogeneous ink. Citrate-stabilized reducing agent solution was prepared by dissolving sodium citrate dehydrate (200 mg) and sodium borohydride (43 mg) in DI water (50 mL) and was then added to the precursor solution under vigorous stirring. Subsequently, the CNT ink was mixed into the as-prepared PdAu hydrosol. In order to facilitate the deposition of PdAu nanoparticles onto the CNT support, 0.4 M potassium sulfate solution (150mL) was slowly pumped into the aforementioned mixture in 12 hr. After filtrated and dried in the vacuum oven at room temperature overnight, PdAu/CNT catalyst with a loading of 20 wt% was obtained.

**Physical characterization of Au/CNT, Pd/CNT and PdAu/CNT catalysts**

The structure, composition and morphology of Au/CNT, Pd/CNT and PdAu/CNT catalysts were characterized by X-ray diffraction (XRD), and transmission electron microscopy (TEM). Scintag XDS-2000 θ/θ diffractometer (Cu Kα radiation (λ = 1.5406 Å) with 35 mA filament current and 45 kV tube voltage) were employed to collect XRD patterns at a
continuous scan rate of 1.2 degree per minute. The mean crystallite sizes of Au/C-NC and Au/C-AQ catalysts are calculated using the (220) peak based on Debye-Scherrer formula:

\[
L = \frac{0.9 \lambda_{K\alpha}}{B_{2\theta} \cos \theta_{\text{max}}}
\]

(1)

where \(L\) is the mean crystal size, \(\lambda\) is the wavelength of the x-ray (1.5406Å), \(B\) is the full width at half-maximum of the peak (rad) and \(\theta_{\text{max}}\) is the Bragg angle (rad) of Au (220).

The transmission electron microscopy (TEM) image of Au/C was collected on JEOL JEM-4000FX with an operating voltage of 200 kV.

**Membrane electrode assembly (MEA) fabrication**

The anode catalyst ink was made by mixing Au/CNT, Pd/CNT and PdAu/CNT catalyst power, 5 wt% PTFE in water suspension into iso-propanol (10 mg\text{catalyst/ml}, mass ratio PTFE:catalyst=5:95), and sprayed onto a carbon cloth (PTFE-untreated, 381 μm, Fuel Cell Store) that serves as the liquid diffusion layers (LDL) to achieve a loading of 1.0 mg\text{Au cm}^{-2}. The cathode catalyst ink (10 mg\text{catalyst/ml}, mass ratio ionomer:catalyst=3:7), which was made from 1-propanol dispersion of a commercial non-precious metal HYPERMECTM (Fe-Cu-based catalyst, Acta 4020) blended with an AS-4 a non-conductive ionomer (Tokuyama), was airbrushed directly onto the AEM. Carbon paper (Toray) was employed as the cathode gas diffusion layer. The evenly-sprayed carbon cloth anode and catalyst coated membrane (CCM) cathode were dried in air under room temperature overnight before use. The MEA was fabricated by directly assembling the anode, cathode and carbon paper in sequence without hot press.
Anion exchange membrane fuel cells (AEM-DGFCs) test and product analysis

Electro-catalytic oxidation of glycerol in AEM-DGFC was conducted on a Scribner fuel-cell test stand (850e). The fuel cell fixture was purchased from Fuel Cell Technology Inc. with an active area of 5 cm². The end plate was modified with stainless steel (316L) to tolerate the alkaline operation environment. During each run, 30 ml of glycerol + KOH solution was introduced into a plastic vessel and pumped into the anode at a flow rate of 1.0 or 4.0 ml min⁻¹ through a closed loop by a peristaltic pump (Gilson Minipuls 3), while the high-purity O₂ (>99.999%) was fed into the cathode compartment at a flow rate of 0.1 or 0.4 L min⁻¹ under a backpressure of 30 or 0 psig. The electro-oxidation was carried out by controlling the fuel cell voltage of 0.1 V. during the reaction, the anode potentials were monitored by a Hg/HgO/1.0 M KOH reference electrode and converted to reversible hydrogen electrode (RHE) by V vs. RHE = V measured vs. Hg/HgO/1.0 M KOH + 0.098+0.059×(pH of electrolyte solution). Hg/HgO/1.0 M KOH reference electrode was calibrated against RHE (HydroFlex®) in a fresh prepared 1.0 M KOH electrolyte at the end of each test, and their potential difference was maintained 0.924 ± 0.007 V in all of the experiments. Samples were removed periodically and analyzed by HPLC using a column (Alltech, OA-1000) with a refractive index detector (RID, Agilent G1362A) and a variable wavelength detector (VWD, 220 nm, Agilent G1314A). An eluent of 5 mM aqueous sulfuric acid at a flow rate of 0.3 ml min⁻¹ were applied for the product separation. 20 µl of sample was injected into the HPLC system. Products were identified by comparison with authentic samples.

The product selectivity/yield and glycerol conversion are calculated by the following equations:
Half cell test

Half cell tests were performed in a conventional three-electrode-cell setup, equipped with a glassy carbon working electrode, and Hg/Hg (1.0 M KOH) reference electrode and a Pt wire counter electrode. Before each test, 20 µl of the 2.0 mg ml\(^{-1}\) catalyst ink was then drop-casted on the glass carbon electrode. Prior to tests, all the electrolytes were deacerated by purging with N₂ gas (99.99%) for 30 min. Ten cyclic voltammograms (CVs) were recorded for Au/CNT, Pd/CNT and PdAu/CNT catalyst and the stabilized polarization curve obtained from the last cycle as reported. All potentials were reported with respect to RHE.

\[
\text{Selectivity of one } C_2 \text{ or } C_3 \text{ product} = \frac{\text{moles of } C_2 \text{ or } C_3 \text{ product}}{\text{total moles of } C_2 \text{ and } C_3 \text{ products}} \times 100\% \tag{2}
\]

\[
\text{Conversion of glycerol} = (1 - \frac{\text{concentration of glycerol at certain time}}{\text{Initial concentration of glycerol}}) \times 100\% \tag{3}
\]

\[
\text{Yield of } C_2 \text{ or } C_3 \text{ product} = \text{selectivity of } C_2 \text{ or } C_3 \text{ product} \times \text{conversion of glycerol} \tag{4}
\]
4.2.4 Results and discussion

**Figure 4.9** Cyclic voltammograms of Pd/CNT, PdAu/CNT, and Au/CNT for glycerol oxidation in N₂ purged 1.0 M KOH + 0.1 M glycerol at 50 mV s⁻¹, room temperature.

Cyclic voltammograms were conducted to study electrocatalytic oxidation of glycerol, glycerate, tartronate and mesoxalate over Pd/CNT, PdAu/CNT, and Au/CNT catalysts. Compared with Au/CNT and Pd/CNT, PdAu/CNT has the most negative onset potential (0.58 V) and highest current density within the fuel cell anode potential window (1.74 mA cm⁻² at 0.7 V for example) for GOR, as shown in Figure 4.8. Therefore, the synergetic effect of PdAu/CNT will improve the total reaction rate of glycerol oxidation reaction network, leading to higher glycerol conversion (unit time) and power output than monometallic Au/CNT and Pd/CNT in the single cell the power output.
Figure 4.10 Cyclic voltammograms of Pd/CNT, PdAu/CNT, and Au/CNT for glycerate oxidation in N₂ purged 1.0 M KOH + 0.1 M glycerate at 50 mV s⁻¹, room temperature.

Compared with Au/CNT and Pd/CNT, PdAu/CNT has the most negative onset potential (0.53 V) and highest current density (0.30 mA cm⁻² at 0.7 V for example) within the fuel cell anode potential window, see Figure 4.9, within which Au/CNT can not obviously catalyze glycerate oxidation reaction. Although not as fast as PdAu/CNT, Pd/CNT also has the ability to oxidize glycerate when the applied anode potential is less than 0.7 V. From the whole glycerol oxidation network aspect, Au active site is helped by Pd active site to accelerate the consecutive oxidation of glycerate as reaction intermediate, taking advantage of the synergic effect.
Figure 4.11 Cyclic voltammograms of Pd/CNT, PdAu/CNT, and Au/CNT for tartronate oxidation in N₂ purged 1.0 M KOH + 0.1 M tartronate at 50 mV s⁻¹, room temperature.

As shown in Figure 4.10, desorbed tartronate in the bulk electrolyte is quite stable the whole scan range (including fuel cell anode potential window < 0.7 V), making tartronate an ideal high yield dead end product. It is noteworthy that the double layer charge of Pd/CNT is higher than the corresponding part of Au/CNT and PdAu/CNT, which can be attributed to its smaller particle size (Figure. 4.S1 and Figure. 4.S2) and thus better dispersion on the surface of the glassy carbon electrode.
As an end product as well as a reaction intermediate, any further oxidation of $C_3$ mesoxalate will result in C-C bond cleavage. Mesoxalate is relatively stable on gold catalyst without generating notable current density at $<0.7\ \text{V}$ (see Figure 4.11), indicating Au can protect C-C cleavage originated from mesoxalate consecutive oxidation. The higher palladium atomic ratio in the catalyst (0% for Au/CNT, 50% for PdAu/CNT and 100% for PdAu/CNT), the higher activity the catalyst is towards mesoxalate oxidation and thus more C-C cleavage of $C_3$ mesoxalate to $C_2$ and $C_1$ products such as oxalate and carbonate.
Figure 4.13 Electro-catalytic selective oxidation of glycerol on Au/CNT (20 wt%) in AEM-DGFC under optimized condition for high yield of tartronate. Anode catalyst: Au/CNT Cathode catalyst: Fe-Cu-based catalyst (Acta 4020), anion exchange membrane (A901, Tokuyama Inc.). Anode fuel: 8.0 M KOH + 1.0 M glycerol, 30 ml, 1.0 ml min⁻¹; Cathode fuel: high purity O₂, 100 ml min⁻¹, ambient pressure. Glycerol:Metal = 1:1000 (mol:mol); Cell voltage: 0.1 V; Cell temperature: 60 °C reaction time: 8 h.
Electro-catalytic selective oxidation of glycerol on Au/CNT, Pd/CNT and PdAu/CNT (20 wt%) in AEM-DGFC under optimized condition are shown in Figure 4.12-14. Selectivity of glycerate and tartronate does not obviously change with time, indicating that deeper oxidized products mainly come from the direct oxidation of adsorbed glycerol (C₃ species) on the catalyst. After desorption, glycerate and tartronate are hard to be re-adsorbed and get further oxidized on Au catalyst. Therefore, glycerate and tartronate are possible dead-end products of glycerol oxidation on Au catalyst.

The anode potential range is 0.3 V - 0.5 V, which indicates the meaningful potential window for a DGFC in half cell cyclic voltammetry. The anode potential increases in the 8 h constant voltage operation due to the increase of conversion. The higher the conversion is, the lower the fuel concentration will be. Therefore, when the conversion is higher, the anode side of fuel cell consumes more overpotential.

The problem of Au/CNT is that the glycerol oxidation reaction in highly inhibited by the generated reaction products, leading to a slow reaction rate especially when the conversion of glycerol is high. Furthermore, since Au/CNT does not have a strong ability catalyzing the further oxidation of reaction intermediate glycerate, the yield of target product tartronate is hard to be maximized.
Figure 4.14 Electro-catalytic selective oxidation of glycerol on Pd/CNT (20 wt%) in AEM-DGFC under optimized condition for high yield of tartrionate. Anode catalyst: Pd/CNT Cathode catalyst: Fe-Cu-based catalyst (Acta 4020), anion exchange membrane (A901, Tokuyama Inc.). Anode fuel: 8.0 M KOH + 1.0 M glycerol, 30 ml, 1.0 ml min\(^{-1}\); Cathode fuel: high purity O\(_2\), 100 ml min\(^{-1}\), ambient pressure. Glycerol:Metal = 1:1000 (mol:mol); Cell voltage: 0.1 V; Cell temperature: 60 °C reaction time: 8 h.
As comparison, the selectivity of glycerate decreases while that of tartronate and oxalate increase with time, revealing that the desorbed glycerate in the bulk electrolyte can be re-adsorbed and get further oxidized, leading to higher selectivity and yield to tartronate. The selectivity of C₂ oxalate on Pd/CNT catalyst is higher than that on Au/CNT, since the C-C bond cleavage for C₃ species occurs more severely on Pd than on Au.

So as to maximize the selectivity and yield of target product, tartronate, it is not only necessary to accelerate the re-adsorption and further oxidation of reaction intermediate glycerate by Pd active sites, but also important to protect the C-C bond of C₃ species by Au active sites, which is the design rationale of PdAu alloyed catalysts for selective oxidation of glycerol to tartronate.
Figure 4.15 Electro-catalytic selective oxidation of glycerol on PdAu/CNT (20 wt%) in AEM-DGFC under optimized condition for high yield of tartronate. Anode catalyst: PdAu/CNT Cathode catalyst: Fe-Cu-based catalyst (Acta 4020), anion exchange membrane (A901, Tokuyama Inc.). Anode fuel: 8.0 M KOH + 1.0 M glycerol, 30 ml, 1.0 ml min⁻¹; Cathode fuel: high purity O₂, 100 ml min⁻¹, ambient pressure. Glycerol:Metal = 1:1000 (mol:mol); Cell voltage: 0.1 V; Cell temperature: 60 °C reaction time: 8 h.
As depicted in Figure 4.14, over bimetallic PdAu/CNT anode catalyst, with the highest power out generated (43.7 mW cm\(^{-2}\) at 1 h for instance), the yield of tartronate increased from 25.9 % to 68.4 % while that of glycerate decreased from 6.44 % to 1.35 % within the 8 h reaction time, confirming the three major synergetic effects of palladium and gold that maximize tartronate yield and power density. Firstly, desorbed glycerate can be re-adsorbed and consecutively oxidized on Pd but not on Au in fuel cell anode potential range (< 0.7 V vs. RHE). The sequential oxidation of the second primary hydroxyl group on Pd helps the bimetallic catalyst to minimize the unwanted glycerate yield as a reaction intermediate. Secondly, Au helps the bimetallic catalyst to protect the C-C bond of C\(_3\) species, alleviating the GOR from producing high yield of C\(_2\) oxalate. Thirdly, the reaction rate on the bimetallic PdAu/CNT is faster than that on Au/CNT and Pd/CNT, leading to a higher energy output and glycerol conversion in unit time.
Figure 4.16 Proposed reaction pathway for main C₃ partial oxidation products on Pd/CNT, PdAu/CNT, and Au/CNT in alkaline media. All pathways are based on desorbed species in bulk electrolyte under current testing configurations.

Figure 4.15 illustrates the proposed reaction pathway for glycerol and main C₃ partial oxidation products over Pd/CNT, Au/CNT, and PdAu/CNT. Since tartronate has little activity over Au/CNT, Pd/CNT, and PdAu/CNT from 0 - 1.2 V (Figure 4.10), the generated mesoxalate does not come from consecutive oxidation of desorbed tartronate, revealing a hidden pathway from direct glycerol oxidation or glycerate oxidation via adsorbed intermediates. Similarly, the glycerate in the bulk electrolyte has no activity on Au/CNT catalyst (Figure 4.9) but the yield of tartronate reaches 41% over it, indicating another hidden pathway from direct glycerol oxidation via adsorbed C₃ intermediates. Different from Au, Pd active site can consecutively oxidize desorbed glycerate in the bulk electrolyte, making it a vital component to maximize the tartronate yield.
4.2.5 Conclusions

Electrocatalytic selective oxidation of glycerol over bimetallic PdAu supported on CNT (PdAu/CNT) yielded 68.4 % of potassium tartronate (fuel:catalyst molar ratio is 1000) in 5 cm² AEM-DAFC, which is higher than that over Au/CNT (41.0 %) and Pd/CNT (62.0 %). Three major synergetic effects of palladium and gold are found to be able to maximize tartronate yield. Firstly, desorbed glycerate can be re-adsorbed and consecutively oxidized on Pd but not on Au in fuel cell anode potential range (< 0.7 V vs. RHE). The sequential oxidation of the second primary hydroxyl group on Pd helps the bimetallic catalyst to minimize the unwanted glycerate yield as a reaction intermediate. Secondly, Au helps the bimetallic catalyst to protect the C-C bond of C₃ species, alleviating the GOR from producing a high yield of C₂ oxalate. Thirdly, the reaction rate on the bimetallic PdAu/CNT is faster than that on Au/CNT and Pd/CNT, leading to a higher energy output and glycerol conversion in unit time. Our work provides new insights into the synergistic effects over bimetallic PdAu catalysts, and also indicates that one strategy for active site design of electrocatalyst is to integrate different elements (e.g. Pd and Au), which have different activities toward different reaction intermediates (e.g. glycerate, tartronate and mesoxalate) and the initial reactant (e.g. glycerol).
4.2.6 Supporting information

**Figure 4.S1** Bright field transmission electron microscopy (TEM) images of a) Pd/CNT, b) Au/CNT, (c) PdAu/CNT (20 % total metal loading).

**Figure 4.S2** XRD patterns of Pd/CNT, PdAu/CNT, Au/CNT (20 % total metal loading).
4.2.7 References


CHAPTER 5 THEORY GUIDED ELECTROCATALYSTS DESIGN (C-H BOND ACTIVATION)

5.1 Ag-catalyzed Aldehyde Oxidation Facilitating Alcohol Oxidation: Electrocatalyst Design and Homogeneous Reaction Heterogenization by Orbital Energy Difference Matching

5.1.1 Graphical abstract

Figure 5.1 Graphical abstract of section 5.1.

This chapter is adapted from a submitted paper (Ji Qi, Neeva Benipal, David J. Chadderdon, Xiaotong H. Chadderdon, Changhai Liang, Wenzhen Li, PdAg/CNT Catalyzed Alcohol Oxidation Reaction Facilitated by Ag Catalyzed Aldehyde Oxidation Reaction for High-Performance Anion Exchange Membrane Direct Alcohol Fuel Cell (Alcohol = Methanol, Ethanol, Ethylene Glycol and Glycerol)). This research reported PdAg bimetallic catalysts can
effectively improve the overall alcohol oxidation rate (fuel cell power density) and increase faradaic / fuel efficiency (high selectivity to deep oxidation products) of direct alcohol fuel cell. We first proposed a theoretical descriptor to screen and predict the catalytic activity of different active sites, followed by confirming the calculation with experiments. Orbital energy difference matching is proposed as a descriptor for electrocatalyst design and homogeneous reaction heterogenization. Combining different heterogenized active sites with well-directed high activity towards original substrate or reaction intermediates is proposed as a strategy for designing multi-functional electrocatalysts improved by spillover of reaction intermediates. Through using various aldehyde and alcohol containing organic molecule as substrates, we clarified that Ag is unique to enhance intermediate aldehyde oxidation to carboxylic acid, and the main role of Pd is to facilitate dehydrogenation of alcohol group to aldehyde intermediate. Although the synergetic effect between Pd and Ag may also contribute to activity enhancement of the dehydrogenation step in AOR, the detailed mechanisms and insights should be clarified in the future research by using electrochemical In-situ spectroscopy and theoretical DFT calculation.

5.1.2 Abstract

PdAg supported on carbon nanotube (PdAg/CNT) with 2.7 nm average particle size are prepared by aqueous phase reduction method for alcohol oxidation reaction in direct alcohol fuel cells. The addition of Ag boosts alcohol oxidation reaction by facilitating aldehyde oxidation reaction. In half-cell system with three electrodes, the peak mass activity of PdAg/CNT reaches 0.105 mA µgPd⁻¹, 0.305 mA µgPd⁻¹, 2.105 mA µgPd⁻¹ and 8.53 mA µgPd⁻¹ for methanol oxidation reaction, ethanol oxidation reaction, ethylene glycol oxidation reaction and glycerol oxidation reaction in 1 M KOH 0.1 M alcohol electrolyte, which are higher than
the mass activity of Pd/CNT at the same applied potential. With PdAg/CNT (0.5 mgPd per MEA - 1) as anode catalyst, direct methanol fuel cell, direct ethanol fuel cell, direct ethylene glycol fuel cell and direct glycerol fuel cell achieve peak power densities of 135.1 mW cm -2, 202.3 mW cm -2, 245.2 mW cm -2 and 276.2 mW cm -2, with corresponding peak mass activities of 270.2 mW mgPd per MEA -1, 404.6 mW mgPd per MEA -1, 490.4 mW mgPd per MEA -1 and 552.4 mW mgPd per MEA -1 at 80 °C and ambient pressure. PdAg/CNT also improves the fuel efficiency of glycerol oxidation by contributing to the C-C bond cleavage of C3 glycerol to C2 oxalate.

5.1.3 Introduction

People are forced to replace limited fossil fuels with renewable and clean energy source to alleviate the environmental pollution and global climate change. [1] The easy handling and large volumetric energy density of alcohol make direct alcohol fuel cells (DAFCs) a potential solution to the current energy issues. [2] Anion exchange membrane DAFCs (AEM-DAFCs) are attracting increasing research efforts as a result of the fast kinetics of anode alcohol oxidation reaction (AOR) and cathode oxygen reduction reaction (ORR) in alkaline media. [3] Although non-precious iron-based catalyst [4-6] or carbon based metal-free catalyst [7, 8] can be used for ORR at cathode side in anion exchange membrane fuel cells (AEMFCs), high loading precious metal is still required for AOR at the anode side in low-temperature AEM-DAFCs. As a result, the cost of catalyst layer takes up more than 50 % in the total cost of AEM-DAFCs[9], which is a major technical obstacle hindering the commercialization of AEM-DAFCs. To overcome this issue, there is urgent need to develop catalyst with large electrochemically active surface area (ECSA), high mass activity and intrinsic activity.

Platinum-based catalysts are the most widely used catalysts in low-temperature DAFCs (< 100 °C). [9, 10] Although Pt’s catalytic activity towards methanol oxidation reaction (MOR)
ethanol oxidation reaction (EOR) [12], ethylene glycol oxidation (EGOR) [13] and glycerol oxidation reaction (GOR) [14] can be very high in DAFCs, its scarcity leads to its high price (> $50 g⁻¹). To reduce the cost of catalyst layer, one method is to lower down the loading of Pt, another method is to replace Pt with Pd, which is more abundant and less expensive. To prepare highly active Pd-based catalysts, a number of strategies have been investigated, such as controlling the morphology of Pd [15-19], alloying other elements to prepare Pd-M catalyst [20-25], and improving the surface area of the catalyst support [26-28]. However, since Pd based catalysts’ activity and the ability to cleave C-C bond for long chain alcohol have to be further improved, there is an urgent need not only to increase the mass activity but also to increase the intrinsic activity of Pd-based anode precious metal catalysts.

In the electrochemical AOR process, carbonyl groups are detected by infrared spectroscopy (IR)[29-32] on the surface of electrodes while carboxylic groups are detected by high-performance liquid chromatography (HPLC) in the liquid electrolyte containing reaction products[5, 33, 34]. The aldehyde is considered either as an intermediate or as a reaction product of electrocatalytic AOR. [35-40] Thus, a faster reaction rate of electrocatalytic aldehyde oxidation reaction (ADOR) contributes to the acceleration of AOR, leading to a higher electricity output. To study electrocatalytic ADOR, previous researchers have successfully used bulk metal anodes [41], Au nanoparticles[42] and Pd nanoparticles supported on carbon nanotube (Pd/CNT) [43] for formaldehyde (C₁ aldehyde) oxidation reaction. However, as C₂+ alcohols have other C₂+ aldehydes as AOR reaction intermediates, activities of different supported nanoparticles towards various aldehydes still require comparison to find an active site facilitating AOR by accelerating ADOR for high-performance DAFCs fed with fuels such as methanol, ethanol, ethylene glycol and glycerol.
In this work, alloyed PdAg nanoparticles supported on carbon nanotubes (PdAg/CNT) were prepared for AOR with an aqueous-phase reduction method excluding the usage of surfactant, which offered several advantages. First, Ag/CNT electrochemically catalyzes the ADOR more efficiently than Pt/CNT, Pd/CNT, and Au/CNT. Pd is a well-known electrocatalyst for AOR, but not the best one for ADOR. Although Ag has little activity towards AOR in alkaline media, it can help other active sites such as Pd to accelerate the reaction rate of ADOR and thereby the whole AOR network. Second, by alloying Pd with Ag, the particle size of Ag can be greatly reduced from 17.7 nm (Ag/CNT) to 2.7 nm (PdAg/CNT) without covering the catalyst’s surface with surfactants, leading to a high ECSA for both Pd and Ag components. Third, PdAg/CNT can also cleave the C-C bond of long chain polyol such as glycerol, providing a high fuel efficiency. Fourth, the carbon nanotube (CNT) support with high electrical conductivity, impressive mechanical and thermal stabilities [44] will form 3 dimensional electrode structure on the membrane electrode assembly (MEA) and enhance the mass transport of alcohol and OH⁻, resulting in an even higher catalyst utilization ratio in actual fuel cell operation. In three electrode half-cell system, the peak mass activity of PdAg/CNT reaches 0.105 mA µgPd⁻¹, 0.305 mA µgPd⁻¹, 2.105 mA µgPd⁻¹ and 8.53 mA µgPd⁻¹ for MOR, EOR, EGOR and GOR in 1 M KOH 0.1 M alcohol electrolyte, respectively. With PdAg/CNT (0.5 mgPd per MEA⁻¹) as anode catalyst, the AEM-DAFC can achieve peak power densities (PPD) of 135.1 mW cm⁻², 202.3 mW cm⁻², 245.2 mW cm⁻² and 276.2 mW cm⁻², with corresponding peak mass activities of 270.2 mW mgPd per MEA⁻¹, 404.6 mW mgPd per MEA⁻¹, 490.4 mW mgPd per MEA⁻¹ and 552.4 mW mgPd per MEA⁻¹ at 80 °C and ambient pressure, when using methanol, ethanol, ethylene glycol and glycerol as fuel respectively.
5.1.4 Experimental section

Chemicals:

The short multi-walled CNT (10-20 nm outer diameter, 0.5-2 μm length) was purchased from Cheaptubes Inc. H₂PtCl₆•xH₂O (~38% Pt basis), Pd(NO₃)₂•2H₂O (~40% Pd basis), AuCl₃ (99%), AgNO₃ (99%), potassium sulfate (99%), polytetrafluoroethylene water solution (60%), potassium hydroxide (85%), 1-propanol (99.5%), methanol (99.8%), ethanol (99.5%), ethylene glycol (99.8%) and glycerol (99.5%) were bought from Sigma-Aldrich Co. The catalyst 4020 was ordered from Acta, Inc. Sodium borohydride (99%) and sodium citrate dihydrate (99%) were manufactured by Acros Organics. All the chemicals were used as received without further purification.

Preparation and physical characterization of different catalysts with X-ray diffraction (XRD) and transmission electron microscopy (TEM)

All the monometallic and bimetallic catalysts including Pt/CNT, Pd/CNT, Au/CNT, Ag/CNT, PdAg/CNT, PdAg₃/CNT (20 % metal loading) were prepared by aqueous-phase reduction method. In a typical process of Pt/CNT for example, the catalyst precursor was dissolved in citric acid water solution firstly. Then the reducing agent solution was prepared by ultrasonically dissolving sodium borohydride into a citric acid water solution. The precursor solution was quickly poured into the reducing agent solution under vigorous stirring, leading to a hydrosol solution of nanoparticles. Both catalyst precursor and sodium borohydride reducing agent were stabilized by citric acid so that the reducing process was controlled at an appropriate rate which ensures that the size of the nanoparticles is small enough for a large surface area. Without adding citric acid, the sodium borohydride would decompose to hydrogen so the
catalyst precursor would not be fully reduced. Short CNTs functionalized by carboxylate acid groups were sonicated in water for 15 min with shaking. The CNTs water mixture was added into the hydrosol solution immediately after the reduction of the precursor, followed by dropwise adding potassium sulfate solution for 12 h into the mixture to facilitate the deposition of nanoparticles. The carboxylic acid groups make CNTs more hydrophilic leading to their better dispersion in water. Therefore, the as-prepared nanoparticles hydrosol can have a better contact with the CNT supports during deposition. After being filtrated and dried in the vacuum oven at room temperature overnight, Pt/CNT catalyst with a loading of 20 wt% was obtained.

The structure and morphology of all the catalysts were characterized by X-ray diffraction (XRD), and transmission electron microscopy (TEM). Scintag XDS-2000 θ/θ diffractometer employed to collect the XRD patterns has Cu Kα radiation (λ = 1.5406 Å) operated under 35 mA filament current and 45 kV tube voltage with a continuous scan rate of 1.2 degree per minute. Due to its relative isolation, the (220) peak is selected to calculate the mean crystallite sizes of all the catalysts based on Debye-Scherrer formula:

$$L = \frac{0.9\lambda_{K\alpha}}{B_{2\theta} \cos \theta_{max}}$$  \hspace{1cm} (1)

where \(L\) is the mean crystallite size, \(\lambda\) is the wavelength of the x-ray (1.5406Å), \(B\) is the full width at half-maximum of the peak (rad) and \(\theta_{max}\) is the Bragg angle (rad) of the (220) peak. The transmission electron microscopy (TEM) images were collected on JEOL JEM-4000FX with an accelerating voltage of 200 kV.
Electrocatalytic activities of different catalysts towards alcohol and aldehyde oxidation in three electrode half-cell system

A three-electrode, water jacket integrated glass cell (AFCELL3, Pine Instrument) including 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) was employed to run cyclic voltammetry (CV) tests. After being shaken in an ultrasonic ice-water bath for 2 min, 2.5 mg catalyst in 4.0 mL 1-propanol and 1.0 mL DI water formed a uniform black colored catalyst ink with a concentration of 0.5 mg mL\(^{-1}\). The DI water improves dispersion of CNT supports with hydrophilic carboxylic acid groups. The catalyst ink was added dropwise onto the surface of the glassy carbon electrode (GCE) with a glass syringe. For monometallic catalyst, the weight of metal on the GCE was 1 µg. For PdAg bimetallic catalyst, the weight of Pd on the GCE was 1 µg since silver is relatively cheap and inactive toward alcohol oxidation within the fuel cell anode potential. 1.0 M potassium hydroxide (KOH) and 0.1 M aldehyde or alcohol was used as electrolyte for the CV tests. With a scan rate of 50 mV s\(^{-1}\), the CV tests were conducted at room temperature under nitrogen atmosphere.
Typical core criteria for catalysts evaluation includes activity, selectivity, durability and reaction conditions, among which turnover frequency (TOF) is the most important parameter reflecting catalyst’s intrinsic activity. \( \text{TOF}_e \) is defined with respect to transferred electrons as instead of converted substrates as follows:

\[
\text{TOF}_e = \frac{I}{F \times \text{ECSA} \times m \times \text{SAD}}
\]

I is the current in the external circuit; \( F \) is Faraday constant; ECSA is the electrochemically active surface area; \( m \) is the mass of metal catalyst on the electrode; SAD is the surface atomic density of difference facets (Supporting Information, Table 5.S7).

\[
\text{ECSA} = \frac{Q_{ox}}{m \times q_{coulombic}}
\]

\( Q_{ox} \) is the integrated charge of the metal oxide reduction peak, \( m \) is the mass of the metal catalyst deposited onto the electrode, and \( q \) is the coulombic charge of different reduction peaks corresponding to the scan range. The ECSA of Pt/CNT[45], Pd/CNT[46], Au/CNT[47] and Ag/CNT[48] was calculated according to coulombic charge of 0.420 mC cm\(^{-2}\), 0.385 mC cm\(^{-2}\), 0.245 mC cm\(^{-2}\) and 0.400 mC cm\(^{-2}\), respectively. (Supporting information, Figure 5.S1)

**Direct alcohol fuel cells with Pd-based anode catalysts**

The fuel cell test stand (850e Scribner-Associates) was operated in scan current mode to collect polarization curve within 0 to 5 A current range. The experiments were performed under ambient pressure and at various temperatures without setting any vertex current. The fuel cell temperature was controlled by feedback loop composed of electric heating rods and a thermocouple thermometer in the stainless steel end plates. The anode catalyst ink (10 mg catalyst
cm\(^3\) concentration) was prepared by mixing catalyst and polytetrafluoroethylene (PTFE) (95:5 mass ratio) in iso-propanol solvent by ultra-sonication in an ice-water bath for 10 min with shaking. The cathode catalyst ink containing 30 wt\% of ionomer (AS4 Tokuyama) as binder and anion conductor was prepared similarly as the anode catalyst ink using 1-propanol as solvent. The Pd loading on the anode catalysts-coated carbon cloth was controlled to be 0.5 mg cm\(^{-2}\) by alternately weighing and spraying the anode catalyst ink onto the carbon cloth substrate. The cathode catalysts coated anion exchange membrane was fabricated by airbrushing 3 mg cm\(^{-2}\) of the cathode catalyst (4020 Acta) onto an anion exchange membrane (A901 Tokuyama). The 5 cm\(^2\) membrane electrode assembly (MEA) was prepared by combining standalone anode (catalysts coated carbon cloth), integrated cathode and anion exchange membrane (catalysts coated anion exchange membrane with carbon paper as backing layer). The MEA was placed between two serpentine graphite flow field plates, which were further pressed by two gilded plate current collectors from both sides. The default testing conditions\(^{[14]}\) were anode fuel: 6.0 M KOH, 3.0 M alcohol, 4.0 ml min\(^{-1}\); cathode fuel: 200 ml min\(^{-1}\) O\(_2\), ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/80/80 °C or 25/60/60 °C.

**Product analysis of GOR in AEM-DGFC with PdAg/CNT anode catalyst**

23.5 ml of 1.0 M glycerol + 6.0 M KOH solution was cycled between a plastic vessel the anode chamber a closed loop by a peristaltic pump (1.0 min\(^{-1}\) flow rate), while the high-purity O\(_2\) (>99.999%) was fed into the cathode compartment at a flow rate of 100 sccm min\(^{-1}\) under ambient pressure. The electrocatalytic GOR was conducted by controlling the fuel cell voltage of 0.2 V. Samples were analyzed by an HPLC using an Alltech, OA-1000 column.
equipped with a refractive index detector (RID, Agilent G1362A) and a variable wavelength
detector (VWD, 220 nm, Agilent G1314A). 5 mM aqueous sulfuric acid eluent at a flow rate
of 0.3 ml min\(^{-1}\) was applied for the product separation. 20 µl of diluted sample (10 times) was
injected into the HPLC system. Products were identified and quantified by comparison with
authentic samples.

The product selectivity, glycerol conversion, and fuel efficiency are calculated by the
following equations:

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

(1)

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

(2)

\[
\varepsilon_f = \varepsilon_e \times X_g = \frac{n_{\text{actual}}}{n_{\text{completely oxidized}}} \times X_g = \frac{Q}{n_{\text{completely oxidized}} m F} \times X_g
\]

\[
= \frac{\int_{t_1}^{t_2} I dt}{n_{\text{completely oxidized}} m F} \times X_g
\]

(3)

where \(S\) is the selectivity of one \(C_2\) or \(C_3\) product; \(X_g\) is the conversion of glycerol; \(\varepsilon_f\) is the
fuel efficiency; \(\varepsilon_e\) is the electron efficiency; \(n_{\text{actual}}\) is the average electrons transferred from a
single glycerol molecule in the electrochemical GOR; \(n_{\text{completely oxidized}}\) (=14) is the electrons
extracted from single glycerol molecule when it is completely oxidized; \(Q\) is the actual charge
integrated from \(I-t\) curve (Figure 5.7); \(m\) is the molar amount of glycerol consumed in the
electrocatalytic GOR; \(t_1\) and \(t_2\) are the reaction time bounds for integration; \(I\) is instantaneous
cell current; \(F\) is Faraday’s constant.
2.6. Supplementary explanations with calculations for Ag’s high activity towards aldehyde oxidation

All the orbital energy calculations were performed with the Gaussian 09 program package. [49] The orbital energy levels and the isosurfaces of the frontier orbitals of aldehydes containing C, H, O atoms (atomic coordinates listed in Supporting information, Table 5.S1-Table 5.S5) were computed at Modified Neglect of Diatomic Overlap (MNDO) [50] level of theory to properly fit the experimental data of ionization energy and electron affinity. Different methods (Austin Model 1 (AM1) method [51] and Parameterized Model number 3 (PM3) method [52]) were used to calculate the chemical hardness to check reproducibility and accuracy by comparing with experimental results (Supporting information, Table 5.S6).
5.1.5 Results and discussion

Figure 5.2 Bright field transmission electron microscopy (TEM) images and corresponding particle size histograms of (a) Pt/CNT, (b) Au/CNT, (c) Pd/CNT, (d) Ag/CNT, (e) PdAg/CNT and (f) PdAg3/CNT.
Figure 5.1 shows the TEM images of carbon nanotube (CNT) supported Pt, Au, Pd, and Ag based catalysts. The average particle size of Pt/CNT, Au/CNT, Pd/CNT, Ag/CNT, PdAg/CNT and PdAg3/CNT measured by randomly counting 100 particles is 1.8 nm, 4.1 nm, 2.5 nm, 17.7 nm, 2.7 nm and 2.8 nm, respectively. The particle size of supported Pd nanoparticles prepared by electroless procedures usually ranges from 3 nm to 25 nm[3]. The aqueous phase reduction method prepared Pd/CNT, PdAg/CNT, and PdAg3/CNT have well-dispersed Pd-based nanoparticles with an average measured particle size less than 3 nm.

Figure 5.3 XRD patterns of Pt/CNT, Au/CNT, Pd/CNT, Ag/CNT, PdAg/CNT and PdAg3/CNT (20% total metal loading) with their particle sizes calculated from (220) diffraction peak.

The XRD patterns of Pt/CNT, Au/CNT, Pd/CNT, Ag/CNT, PdAg/CNT and PdAg3/CNT are depicted in Figure 5.2, with peak position of (1 0 0), (2 0 0), (2 2 0) and (3 1 1) facets marked. The face-centered cubic (FCC) structured Pt/CNT, Au/CNT, Pd/CNT,
Ag/CNT, PdAg/CNT and PdAg$_3$/CNT have mean crystallite size of 1.3 nm, 4.1 nm, 2.0 nm, 13.9 nm, 2.3 nm and 2.4 nm, which were calculated by the full width half maximum (FWHM) method at the Gaussian-fitted (220) peaks using Scherrer's equation. Former researchers have successfully prepared Pd/C [53], Pd-S-HCNF [54], Pd/CNT [55], Pd@WC-Mo2C/C [56], PdSb$_{0.15}$/C [21], PdNi/C [57], PdAg/C[58], and PdAu/C [59] for AOR with mean crystallite size of 4.0 nm, 5.1 nm, 10.5 nm, 6.1 nm, 3.8 nm, 3.1 nm, 3.7 nm and 3.7 nm, respectively. The mean crystallite size of Pd/CNT and PdAg/CNT is further reduced to 2.0 nm and 2.3 nm in the current work by aqueous phase reduction method without using surfactants. The average mean crystallite size determined by XRD is consistent but smaller than the average particle size measured by TEM images. This phenomenon is also found for Pt-based[14, 60], Pd-based [23], and Au-based[61] catalysts, which can be attributed to several possible reasons. First, particles smaller than 0.5 nm are hard to be recognized in TEM images but can be reflected by calculation based on XRD patterns. Second, XRD peak broadening is caused not only by crystallite size but also by factors such as dislocations, stacking faults, twinning, micro stresses, grain boundaries, sub-boundaries, coherency strain, chemical heterogeneities[62]. Third, the mean crystallite size obtained from XRD patterns is single crystal size while the average particle size measured from TEM images includes the agglomeration effect of single crystal particles as a result of intermolecular forces. [58] No obvious phase separation is observed for PdAg/CNT and PdAg$_3$/CNT since alloyed PdAg peaks position between Pd peaks and Ag peaks.
Figure 5.4 Cyclic voltammograms and corresponding TOF$_e$ range in low temperature direct alcohol fuel cell anode potential window (< 0.7 V vs. RHE) of Pt/CNT, Pd/CNT, Au/CNT and Ag/CNT for aldehyde oxidation in N$_2$ purged 1.0 M KOH + 0.1 M formaldehyde (a and b), acetaldehyde (c and d), and glyoxylate (e and f) at 50 mV s$^{-1}$, room temperature.
The mass activity and TOF of Pt/CNT, Pd/CNT, Au/CNT and Ag/CNT towards electrocatalytic aldehyde oxidation are compared with cyclic voltammograms (Figure 5.3 and Table 1). Formaldehyde, acetaldehyde, and glyoxylate are selected as aldehyde substrate because the aldehyde group is easier to be oxidized than the substituent connected to it to ensure that the current generated can properly evaluate the catalysts’ activity for ADOR in the potential range not high enough to oxidize the catalysts. The mass activity and onset potential are two indicators of apparent activity in cyclic voltammetry, while the former is affected by the particle size of catalysts to a larger extent. The highest peak values of mass activity in the forward scan of cyclic voltammograms (Figure 5.3) for formaldehyde oxidation, acetaldehyde oxidation, and glyoxylate oxidation on Pt/CNT (4.6 mA µg\(^{-1}\) at 0.78 V), Au/CNT (0.8 mA µg\(^{-1}\) at 1.06 V) and Pd/CNT (3.3 mA µg\(^{-1}\) at 0.88 V) are positioned at least 400 mV more positive than their corresponding onset potentials (Pt/CNT: 0.33 V; Au/CNT:0.19 V; Pd/CNT: 0.44 V), and are out of the fuel cell anode potential range (from onset potential to < 0.7 V vs. RHE). Taking into account the particle size and potential window mismatch factors, the onset potential is employed as the major indicator of apparent activity rather than (peak) mass activity. Accordingly, due to > 100 mV more negative onset potential (Table 1), Ag/CNT, and Au/CNT are more active than Pd/CNT or Pt/CNT towards aldehyde oxidation. When it comes to intrinsic activity, TOF has been defined as the ratio between the mole amount of converted original substrate and exposed active sites[63, 64]. Herein, to evaluate electrocatalysts’ effectiveness towards series reactions or reaction networks including the original substrate and all the reaction intermediates, the \(TOF_e\) was defined as number of electrons extracted from original reactant or reaction intermediates by each exposed active sites in unit time.
Table 5.1 Apparent and intrinsic activities comparison of different monometallic catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Substrate name and molecular structure</th>
<th>Onset Potential (V vs RHE)</th>
<th>Mass Activity at 0.6 V vs RHE (mA µg⁻¹ metal)</th>
<th>Specific Activity at 0.6 V vs RHE (mA cm⁻² metal)</th>
<th>Turnover Frequency Range for Polycrystalline catalysts at 0.6 V vs RHE (s⁻¹)a</th>
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<tbody>
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<td>1</td>
<td>Pt/CNT</td>
<td>Formaldehyde</td>
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<td>3.085</td>
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<td>Pd/CNT</td>
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<td>0.186</td>
<td>1.703</td>
<td>1.493</td>
<td>6.103 7.048 9.967</td>
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<td>0.018</td>
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<td>0.016</td>
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<td>Ag/CNT</td>
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<td>0.226</td>
<td>0.682</td>
<td>3.551</td>
<td>16.052 18.535 26.212</td>
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</table>

*To evaluate the range of TOF_e for polycrystalline catalysts, it is assumed that the polycrystalline surface can be approximately treated as a linear combination of the major facets. For fcc structure, the minimum, medium and maximum TOF_e can be calculated with surface atomic density of (111), (100), (110) surfaces, respectively.

The $\text{TOF}_e$ of polycrystalline FCC structured Pt/CNT, Pd/CNT, Au/CNT and Ag/CNT is within the range calculated based on (111), (100), and (110) as their major facets (Figure 5.3 and Table 1). At 0.6 V anode potential, the $\text{TOF}_e$ of Ag for ADOR is 1.7–2.2 times, 6.3–45.7 times and 2.2–39.5 times that of Au, Pd, and Pt. The activity sequence of different catalysts toward ADOR is Ag/CNT>Au/CNT>>Pd/CNT and Pt/CNT within the anode potential of fuel cell. We also attempt to screen and explain Ag with high activity towards ADOR using the descriptor of orbital energy difference matching from the energy balance point of view in the charge transfer process. (Supporting information)
However, since the mean crystallite size of Ag (13.9 nm) measured by XRD is 10.7, 7.0 and 3.7 times that of Pt (1.3 nm), Pd (2.0 nm), and Au (3.8 nm) respectively, its electrochemically active surface area (Supporting information, Table 5.S7) and mass activity are relatively low. Pd has high activity and stability toward alcohol oxidation[3], especially in the hydroxyl group deprotonation process, and its particle size is one magnitude smaller than Ag. So as to take advantage of the high TOF_{e^{-}} of aldehyde oxidation on Ag in the ADOR process, the particle size of Ag is controlled by alloying with Pd so that the catalyst’s surface is clean without being covered by capping agents.

Figure 5.5 Cyclic voltammograms of Pd/CNT, PdAg/CNT, PdAg_{3}/CNT and Ag/CNT (baseline, not Pd mass based) for alcohol oxidation in N₂ purged 1.0 M KOH + 0.1 M (a) methanol, (b) ethanol, (c) ethylene glycol, (d) glycerol at 50 mV s⁻¹, room temperature.
In three electrode half-cell system, the peak mass activity of PdAg/CNT reaches 0.105 mA µgPd⁻¹, 0.305 mA µgPd⁻¹, 2.105 mA µgPd⁻¹ and 8.53 mA µgPd⁻¹ for MOR, EOR, EGOR and GOR in 1 M KOH 0.1 M alcohol electrolyte, which are higher than the mass activity of Pd/CNT at the same applied potential. Alloying Pd and Ag reduces the particle size of Ag to less than 3 nm without use of surfactants (Supporting information, Figure 5.1, Table 5.S7), raising the catalyst's activity towards alcohol oxidation reaction network (Figure 5.4) by exploiting spillover of aldehyde intermediates to Ag active sites with high TOF_e⁻ toward aldehyde oxidation. In the electrocatalytic oxidation process of alcohol, some desorbed reaction products are hard to be re-adsorbed and get further oxidized[34]. Altering the active sites by spillover effects before the active reaction intermediates leave the catalyst layer can therefore achieve the deep oxidation of the alcohol. Furthermore, the inertness of Ag towards alcohol oxidation proves that a catalyst is necessary for extracting electrons from the initial deprotonation of a hydroxy group in alkaline media, which is not only a consequence of interactions between hydroxide anions, acidic hydroxyl hydrogen and a conductive electrode surface. As a result, an excessive amount of Ag in a bimetallic catalyst will deteriorate initial deprotonation of hydroxyl groups by diluting and blocking Pd active sites, as depicted in Figure 5.4.
Figure 5.6 Polarization and power density curves of direct alcohol AEMFCs with different anode catalysts (Pd/CNT, PdAg/CNT and PdAg₃/CNT, 0.5 mgₚd cm⁻²) at optimized operating conditions. AEM: Tokuyama A901; cathode catalyst: non-precious metal based catalyst (Acta 4020), 3.0 mgₗcatalyst cm⁻²; anode fuel: 6.0 M KOH + 3.0 M (a) methanol, (b) ethanol, (c) ethylene glycol and (d) glycerol, 4.0 ml min⁻¹; cathode fuel: 200 sccm O₂, ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/80/80 °C.

Ag-catalyzed aldehyde oxidation facilitating alcohol oxidation has a potential application in direct alcohol fuel cells. With PdAg/CNT anode catalyst, low-temperature anion exchange membrane fuel cells (AEMFCs) fueled with methanol, ethanol, ethylene glycol and glycerol have peak power densities of 135.1 mW cm⁻², 202.3 mW cm⁻², 245.2 mW cm⁻², and 276.2 mW cm⁻², which are 23.3 %, 43.2 %, 53.1 % and 53.0 % higher than that of AEMFCs with Pd/CNT as anode catalyst respectively. By diluting and blocking of Pd active sites, an increase in the Ag atomic ratio will suppress the hydroxyl group deprotonation process and
accelerate the aldehyde oxidation processes, which are more effective on Pd and Ag respectively. Influenced by this tradeoff, the total electron release rate of these two processes has a relationship with the Ag atomic ratio (Supporting information, Figure 5.S2). It is noteworthy that the more hydroxyl groups in an alcohol molecule, the larger contribution of Ag facilitated aldehyde oxidation to the total discharge performance will be, owing to the existence of more possible aldehyde intermediates. The performance of AEMFC (Figure 5.5 and Supporting information, Figure 5.S3) with PdAg3/CNT anode catalyst will consequently be closer to that of AEMFCs with PdAg/CNT anode catalyst when the hydroxyl group number per molecule in the substrate increases from 1 (methanol and ethanol) to 2 (ethylene glycol) and to 3 (glycerol).
Figure 5.7 State-of-the-art performances of low temperature (< 100 °C) oxygen or air based DAFCs fed with methanol, ethanol, ethylene glycol and glycerol. Peak power density per mass (Pt, Pd, Au) versus total Pt, Pd, Au loading in the MEA is exhibited for the major DAFCs systems including direct methanol fuel cells (DMFCs) [65-76], direct ethanol fuel cells (DEFCs) [1, 12, 77-118], direct ethylene glycol fuel cells (DEGFCs) [13, 68, 119-122] and direct glycerol fuel cells (DGFCs) [5, 14, 68, 101, 123-125].

Figure 5.6 summarizes the state-of-the-art performances of low temperature (< 100 °C) oxygen or air based DAFCs fed with methanol, ethanol, ethylene glycol, and glycerol. In the current work, the PPDs per mass catalyst reach 270.2 mW mgPd per MEA⁻¹, 404.6 mW mgPd per MEA⁻¹, 490.4 mW mgPd per MEA⁻¹, and 552.4 mW mgPd per MEA⁻¹ for DMFC, DEFC, DEGFC, and DGFC, which are among the highest published results. Although the peak mass activity of DGFC (552.4 mW mgPd per MEA⁻¹) with PdAg/CNT anode catalyst is slightly lower than that (569.2 mW mgPt per MEA⁻¹) of DGFC with surface dealloyed PtCo supported on carbon nanotube (SD-PtCo/CNT) anode catalyst, PdAg/CNT is still a generally cost-effective replacement of Pt for DAFCs.
Figure 5.8 Electrocatalytic selective oxidation of glycerol on Pd/CNT, PdAg/CNT, and PdAg₃/CNT in DGFC for C-C bond cleavage and fuel efficiency analysis. Anode catalyst: Pd/CNT, PdAg/CNT or PdAg₃/CNT (0.5 mg_Pd cm⁻²); Cathode catalyst: non-precious metal based catalyst (Acta 4020, 3 mg cm⁻²), anion exchange membrane (A901, Tokuyama Inc.). Anode fuel: 6.0 M KOH + 1.0 M glycerol, 23.5 ml, 1.0 ml min⁻¹; Cathode fuel: high purity O₂, 100 ml min⁻¹, ambient pressure.; Cell voltage: 0.2 V; Cell temperature: 60 °C or 80 °C reaction time: 2 h or 4 h.

Figure 5.7 shows C-C bond cleavage and fuel efficiency analysis of glycerol (long chain C₃ polyol) oxidation on Pd/CNT, PdAg/CNT and PdAg₃/CNT in DGFC. For 2 h of electrocatalytic GOR in DGFC at 60 °C, the selectivity of C₂ oxalate on Pd/CNT, PdAg/CNT
and PdAg₃/CNT is 8.6 %, 22.8 % and 32.0 % while the corresponding conversion of glycerol is 55.3 %, 49.3 %, and 46.6 %, respectively, indicating that the addition of silver contributes to the C-C bond cleavage of C₃ glycerol to C₂ oxalate and lowers conversion of glycerol. Balancing the tradeoff between the selectivity of C₂ oxalate and conversion of glycerol, DGFC with PdAg/CNT anode catalyst generates the highest current density and fuel efficiency during the electrocatalytic GOR. The fuel efficiency on PdAg/CNT is 28.1 %, which is 4.5 % and 15.2 % higher than that on Pd/CNT and PdAg₃/CNT. After 4 h of GOR at 80 °C on PdAg/CNT anode catalyst, the selectivity of C₂ oxalate, conversion of glycerol and fuel efficiency of GOR further increases to 85.8% and 49.3 %, making PdAg/CNT not only a highly active but also a highly efficient catalyst for GOR and DGFC in alkaline media.

5.1.6 Conclusions

In summary, PdAg/CNT was prepared for AOR in AEM-DAFCs with an aqueous-phase reduction method excluding the usage of surfactant. With PdAg/CNT (0.5 mgPd per MEA⁻¹) as anode catalyst, the AEM-DAFCs achieve PPD of 135.1 mW cm⁻², 202.3 mW cm⁻², 245.2 mW cm⁻² and 276.2 mW cm⁻², with corresponding peak mass activities of 270.2 mW mgPd per MEA⁻¹, 404.6 mW mgPd per MEA⁻¹, 490.4 mW mgPd per MEA⁻¹ and 552.4 mW mgPd per MEA⁻¹ at 80 °C and ambient pressure, when using methanol, ethanol, ethylene glycol and glycerol as fuel respectively. The high activity of PdAg/CNT towards AOR in AEM-DAFCs is attributed to several reasons. First, Ag/CNT electrochemically catalyzes the ADOR more efficiently than Pt/CNT, Pd/CNT and Au/CNT. Although not active towards AOR in alkaline media, Ag helps Pd to accelerate the reaction rate of ADOR and thereby the whole AOR network. Second, by alloying Pd with Ag, the particle size of Ag can be greatly reduced from 17.7 nm (Ag/CNT) to
2.7 nm (PdAg/CNT) without covering the catalyst’s surface by surfactants, leading to a high ECSA for both Pd and Ag components. Third, PdAg/CNT cleaves the C-C bond of long chain polyol such as glycerol, providing a high fuel efficiency. Fourth, CNT support with high electrical conductivity, impressive mechanical and thermal stabilities will form 3 dimensional electrode structure on MEA and enhance the mass transport of alcohol and OH⁻, resulting in an even higher catalyst utilization ratio in actual fuel cell operation. Moreover, it is worth mentioning that the synergetic effect between Pd and Ag may also contribute to the dehydrogenation step in AOR. Detailed mechanisms and insights should be clarified in the future research by using In-situ spectroscopy and DFT calculation.
5.1.7 Supporting information

**Figure 5.S1** Cyclic voltammograms of Pt/CNT, Pd/CNT, Au/CNT and Ag/CNT catalysts in 1.0 M KOH, at 50 mV s$^{-1}$, 25 °C.

**Table 5.S1** Atomic coordinates for formaldehyde.

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**Table 5.S2** Atomic coordinates for acetaldehyde.

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**Table 5.S3** Atomic coordinates for glycolaldehyde.

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Table 5.S6 Comparison of calculated chemical hardness from different methods with the experimental chemical hardness results

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<th>MNDO LUMO energy (eV)</th>
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<th>AM1 LUMO energy (eV)</th>
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<th>PM3 LUMO energy (eV)</th>
<th>HOMO energy (eV)</th>
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^a η is the calculated chemical hardness of aldehyde molecules. ^b η_e is the experimental chemical hardness of aldehyde molecules.
Table 5.S7 Particle size, electrochemically active surface area (ECSA) and surface atomic density of Pt/CNT, Pd/CNT, Au/CNT and Ag/CNT.

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<th>Surface atomic density (nmol cm⁻²)</th>
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Figure 5.S2 The relationship between silver atomic ratio in PdAg bimetallic catalysts and total electron releasing rate reflected by peak power density in direct alcohol fuel cells corresponding to Figure 5.4.
**Figure 5.S3** Polarization and power density curves of direct alcohol AEMFC with different anode catalysts (Pd/CNT, PdAg/CNT and PdAg3/CNT, 0.5 mgPd cm\(^{-2}\)) at optimized operating conditions. AEM: Tokuyama A901; cathode catalyst: non-precious metal catalyst (Acta 4020), 3.0 mgcatalyst cm\(^{-2}\); anode fuel: 6.0 M KOH + 3.0 M (a) methanol, (b) ethanol, (c) ethylene glycol and (d) glycerol, 4.0 ml min\(^{-1}\); cathode fuel: 200 sccm O\(_2\), ambient pressure; temperature (anode fuel/cathode fuel/cell): 25/60/60 °C.

**Explanation of Ag’s high activity toward aldehyde oxidation**

**1. Introduction and background**

After long-time random trial and error at lab scale and massive systematic screening, computational catalyst design employing theory and calculation has become inevitable to shorten the industrialization period of catalysts and lower their development cost. State-of-the-art theory-guided catalyst screening methods have been able to correlate appropriate theoretical
descriptors with experimental activity of different catalysts.[126, 127] Norskov et al. proposed the dissociative adsorption energy as a descriptor and established a volcano-type relationship between it and the reaction rate for methanation reactions [128, 129], ammonia synthesis reactions[130, 131], oxygen reduction reactions[132] and hydrogen evolution reactions[133-135]. Other descriptors such as number of d-electrons[136], enthalpy change[137], reaction barriers[138, 139], p-band center[140] and formation energy[141] can also be used to screen catalysts or to explain their activity differences. Since it is still really challenging to experimentally prove the real elementary steps and rate determining steps for many reactions, it is worth the effort to develop theoretical descriptors and catalyst design strategies that can be linked with the experimental results, taking advantages of factors such as charge transfer and electrode polarization in electrochemical reactions.

Before charge transfer occurs, reactants should have a strong association with catalysts to be easily adsorbed onto the catalysts’ surface, generating electron conducting pathways between active sites and electron sources. To evaluate the intensity of the interaction between different metal ions and ligands, Chatt and Davis classified metal ions into two groups depending on the ligand atoms of their most stable metal complexes.[142] Pearson further classified Lewis acids and bases into ‘hard and soft acid and base’(HSAB) based on their polarizability and proposed the HSAB principle: Hard acids prefer to associate with hard bases, and soft acids prefer soft bases[143], which qualitatively indicates the difficulty of reactant association with the active sites in catalytic reactions. The electron transfer process, another key contributor to electrocatalytic reactions other than the effectiveness of association with reactants, is accompanied by orbital energy transition[144]. If the energy difference between energy levels of the electron donor’s electron orbitals is close to that of the electron acceptor’s
electron orbitals, an electron in excited state from the electron donor is prone to excite the electrons in the electron acceptor from an energy balance point of view. After the excited electron loses its energy in the electron acceptor’s orbital, the electron transfer will be completed, pushing forward the reaction process. In other words, if the energy change when the electron donor loses an electron is close to the energy change when the electron acceptor accepts an electron, the reaction with charge transfer will require less external energy to maintain its continuity, which can be reflected by more negative onset potential and higher intrinsic activity in the experiment. The difference between ionization energy and electron affinity[145] is equivalent to the frontier orbital energy difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)[146, 147], indicating that the energy change in charge transfer process can be theoretically and experimentally linked and quantified. Based on the energy balance in the electron transfer process, it is proposed that the matchup of the orbital energy difference can be used as a descriptor for catalysts’ activities in electrocatalytic reactions with electron transfer.

Polarized by an external electric field, metallic electrode materials are conductive due to the existence of nearly free electrons and the ionic lattice[148, 149], which makes zero oxidation state metals approach their ion states. If their ion state catalytic properties can function before the applied potential is high enough to oxidize them, originally homogeneous reactions can thus be electrochemically heterogenized, which is of great importance because 90% percent of industrialized catalysts are heterogeneous[150]. While homogeneous catalyst heterogenization (HCH) has attracted interest among the industrial community[151-153], electrochemical HCH is different from molecular catalyst immobilization[154, 155] HCH method, which usually anchors organometallic complexes onto support materials to change the
dispersion status of active sites. By electrochemically heterogenizing the active sites, the average distance between adjacent active sites of different functions can be tremendously shortened to lattice spacing level (< 1 nm). The reaction intermediates can thus easily reach the more appropriate active sites by spillover effects[156], facilitating the generation of final products. Before combining well-defined active sites for multi-functional catalysts, it is consequently necessary to heterogenize the reaction to unite the relatively isolated active sites in the corresponding homogeneous reaction and thus realize the synergetic effects of adjacent active sites.

A case in point of electrocatalyst design and HCH with this descriptor is catalyst screening for the aldehyde oxidation reaction (to carboxylic acid), which contains only two electrons transfer, so the effectiveness of the first electron transfer play an important role in evaluating this reaction. The target of the present work is to preliminarily screen catalysts by HSAB principle and orbital energy difference matching, followed by experimentally making zero-valent metals approach their ion-state Lewis acid counterparts via electrode polarization to enhance the adsorption and charge transfer of various Lewis bases (e.g. different aldehydes). This way, originally homogeneous reactions can be electrochemically heterogenized to separate the reactant adsorbent and ultimate electron acceptor, leading to current generation by changing electron pathway to the external circuit. In this work, combining well-defined active sites for intermediate aldehyde oxidation and well-known catalyst alcohol oxidation, the multifunctional bimetallic catalyst was also used as anode catalyst in the direct alcohol fuel cell as an application.
2. Results and discussion

Table 5.8 Calculated orbital energy and chemical hardness of aldehydes with different substituent groups

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<th>HOMO energy (eV)</th>
<th>LUMO energy (eV)</th>
<th>η&lt;sup&gt;a&lt;/sup&gt; (eV)</th>
<th>η&lt;sup&gt;b&lt;/sup&gt; (eV)</th>
<th>E&lt;sub&gt;gap(sub)&lt;/sub&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>(–H)</td>
<td>-11.07</td>
<td>0.94</td>
<td>6.01</td>
<td>6.2</td>
<td>12.02</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>(–CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>-10.88</td>
<td>0.86</td>
<td>5.87</td>
<td>5.7</td>
<td>11.74</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>(–CH&lt;sub&gt;2&lt;/sub&gt;OH)</td>
<td>-11.20</td>
<td>0.38</td>
<td>5.79</td>
<td>N/A</td>
<td>11.58</td>
</tr>
<tr>
<td>Glyceraldehyde</td>
<td>(–CH&lt;sub&gt;2&lt;/sub&gt;OHCHOH)</td>
<td>-10.94</td>
<td>0.45</td>
<td>5.70</td>
<td>N/A</td>
<td>11.40</td>
</tr>
<tr>
<td>Glyoxylic acid</td>
<td>(–COOH)</td>
<td>-11.28</td>
<td>-0.46</td>
<td>5.41</td>
<td>N/A</td>
<td>10.82</td>
</tr>
</tbody>
</table>

<sup>a</sup> η is the calculated chemical hardness of aldehyde molecules; <sup>b</sup> η is the experimental chemical hardness of aldehyde molecules[157]; <sup>c</sup> E<sub>gap(sub)</sub> is the frontier orbital energy difference (HOMO-LUMO gap) of different substrates
The catalyst screening analysis for aldehyde oxidation reaction starts from the acid and base classification of aldehydes. According to the calculation of Mulliken charge distribution[158] (Table 5.S8), the carbonyl group is composed of a carbon atom as an electropositive center (0.220 ~ 0.292 charge) and an oxygen atom as an electronegative center (-0.322 ~ -0.224 charge), indicating that this sp² hybridization structure is highly polarizable, which is a common feature of Lewis soft base. For electrocatalytic oxidation reaction, the nucleophilic oxygen electronegative center connected to the distorted π bond will be gathered near positive terminal such as an anode electrode, facilitating the adsorption of aldehydes. When an aldehyde group is bound to a hydrogen atom (formaldehyde), a methyl group (acetaldehyde), a hydroxymethyl group (glycolaldehyde), 1,2-dihydroxyethyl (glyceraldehyde) and a carboxylic group (glycolic acid) respectively, the calculated chemical hardness for the whole molecule is lower than 6.2 eV, indicating these easily oxidized substrates can be Lewis soft base to form strong covalent bonds with Lewis soft acid. Therefore, the catalysts with strong adsorption of substrate containing aldehyde group should be Lewis soft acids.

Although zero-oxidation-state metals are Lewis soft acids, their frontier orbital energy difference (e.g. 5.74-7.78 eV for zero oxidation state metals in Table 5.S9) is far from the aldehydes’ counterparts (e.g. 10.82-12.02 eV for aldehyde molecules in Table 5.S8). Fortunately, metals can be viewed as nearly free electrons and positive ionic lattice under potential perturbation[148, 149], which makes them conductive. With applied potential, solid zero oxidation state metal electrodes polarized can function as low oxidation state metal ions in heterogeneous electrocatalytic reactions. Without ionization, the non-frontier orbitals of
those metals can be used heterogeneously facilitating charge transfer from reactant molecules. The low oxidation state ions should also be Lewis soft acids (listed in Table 5.S9) to ensure their orbital energy difference match that of aldehyde molecules.

Qualitatively speaking, the electron donor loses electrons and releases energy while the electron acceptor accepts electrons and absorbs energy in the electron transfer process. Since the transition of energy levels requires rigorous energy matching, the closer between the orbital energy difference of electron donor and electron acceptor, the less external energy supply is required to maintain the continuity of the charge transfer process, which is the criterion to further quantitively screen the catalyst. In the electrocatalytic oxidation reactions, electron donor’s electrons first transfer from HOMO to LUMO. After being accelerated by the external potential field, these electrons will excite the outer shell electrons in the electron acceptor’s orbital, followed by losing their energy and staying in the electron acceptor’s orbital. Such an exchange process completes the transfer of electrons between different orbitals, rendering its difficulty reflects the efficiency of different catalysts toward catalyzing the same reaction. As an organic compound with a formyl group as the most easily oxidized functional group, an aldehyde can be oxidized to a carboxylic acid involving transfer of only two electrons. The first electron transfer, represented by frontier orbital energy gap, will thus play an important role in evaluating this reaction.
Table 5.59 Calculated chemical hardness and orbital energy difference of zero and one oxidation state Lewis soft acid metals

<table>
<thead>
<tr>
<th>Element</th>
<th>$A$</th>
<th>$I_{1st}$</th>
<th>$I_{2nd}$</th>
<th>$\eta_0$</th>
<th>$E_{\text{gap0(cat)}}$</th>
<th>$\eta_{+1}$</th>
<th>$E_{\text{gap+1(cat)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
</tr>
<tr>
<td>Ru</td>
<td>1.08</td>
<td>7.36</td>
<td>16.79</td>
<td>3.14</td>
<td>6.28</td>
<td>4.71</td>
<td>9.42</td>
</tr>
<tr>
<td>Rh</td>
<td>1.14</td>
<td>7.46</td>
<td>18.03</td>
<td>3.16</td>
<td>6.32</td>
<td>5.29</td>
<td>10.57</td>
</tr>
<tr>
<td>Pd</td>
<td>0.56</td>
<td>8.34</td>
<td>19.38</td>
<td>3.89</td>
<td>7.78</td>
<td>5.52</td>
<td>11.04</td>
</tr>
<tr>
<td>Ag</td>
<td>1.30</td>
<td>7.58</td>
<td>21.45</td>
<td>3.14</td>
<td>6.28</td>
<td>6.94</td>
<td>13.87</td>
</tr>
<tr>
<td>Cd</td>
<td>-</td>
<td>8.99</td>
<td>16.91</td>
<td>-</td>
<td>-</td>
<td>3.96</td>
<td>7.92</td>
</tr>
<tr>
<td>Os</td>
<td>1.08</td>
<td>8.71</td>
<td>16.58</td>
<td>3.81</td>
<td>7.62</td>
<td>3.94</td>
<td>7.87</td>
</tr>
<tr>
<td>Ir</td>
<td>1.56</td>
<td>9.12</td>
<td>16.58</td>
<td>3.78</td>
<td>7.56</td>
<td>3.73</td>
<td>7.46</td>
</tr>
<tr>
<td>Pt</td>
<td>2.13</td>
<td>9.02</td>
<td>18.56</td>
<td>3.45</td>
<td>6.9</td>
<td>4.77</td>
<td>9.54</td>
</tr>
<tr>
<td>Au</td>
<td>2.31</td>
<td>9.23</td>
<td>20.52</td>
<td>3.46</td>
<td>6.92</td>
<td>5.65</td>
<td>11.29</td>
</tr>
<tr>
<td>Hg</td>
<td>-</td>
<td>10.44</td>
<td>18.76</td>
<td>-</td>
<td>-</td>
<td>4.16</td>
<td>8.32</td>
</tr>
<tr>
<td>Tl$^f$</td>
<td>0.38</td>
<td>6.11</td>
<td>20.43</td>
<td>2.87</td>
<td>5.74</td>
<td>7.16</td>
<td>14.32</td>
</tr>
</tbody>
</table>

$A$ is experimental electron affinity; $I_{1st}$ is experimental first ionization energy; $I_{2nd}$ is experimental second ionization energy; $\eta_0$ is the calculated chemical hardness of 0 oxidation state metal; $E_{\text{gap0(cat)}}$ is the frontier orbital energy difference (HOMO-LUMO gap) of different metal catalysts in their 0 oxidation states; $\eta_{+1}$ is the calculated chemical hardness of +1 oxidation state metals; $E_{\text{gap+1(cat)}}$ is the frontier orbital energy difference of different metal catalysts in their +1 oxidation state, which is not frontier orbital energy difference with respect to the polarized but not oxidized 0 oxidation state metal; $^f$ Tl is highly toxic and not stable in the air so it is excluded from current research.
Quantitively speaking, electron donor’s orbital energy difference should be close to the electron acceptor’s counterpart. For electrocatalytic oxidation reaction occurring at the anode electrode, the electrocatalyst’s frontier or non-frontier orbital energy difference should be close and slightly larger than the electron donor’s frontier orbital energy difference, which is a descriptor evaluating the effectiveness of continuous catalytic charge transfer from an energy balance point of view. Among all Lewis soft acid metals (Table 5.S9), there are four elements, Pd, Au, Ag, and Tl whose first oxidation state ions’ frontier orbital energy differences (11.04 eV, 11.29 eV, 13.87 eV and 14.32 eV) are close to the average (11.44 eV) and larger than the minimum (10.82 eV) of that for aldehyde molecules.
Figure 5.S4 (a) Calculated orbital energy diagram of HOMO−1, HOMO, LUMO, and LUMO+1 for different aldehydes with frontier HOMO-LUMO gaps ($E_{\text{gap(sub)}}$) as orbital energy differences; (b) TOF$^e_-$ (at 0.6 V vs RHE) as a function of orbital energy difference matching represented by $E_{\text{gap+1(cat)}} - E_{\text{gap(sub)}}$. Experimental points of the same substrate are linked with arrows. The solid arrows link points follow an obvious mutual trend, while the dotted ones link points that need further clarifications.
The reason behind the activity sequence is analyzed based on the orbital transition of substrates and catalysts. In all the substrates with different side chains, the frontier orbitals surrounding the aldehyde groups have lodes with similar shapes. The flipping of nodal plane can be observed in all their HOMO→LUMO transition process, in which the HOMO-LUMO gaps of these aldehydes have less than 10 % difference (Figure 5.S4a). Since these different side chains do not lead to significant change in the orbital transition process, they should not cover the mutual trend within the electron transfer of aldehyde oxidation. If the intrinsic activity (TOF_{e-}) is correlated with the degree of orbital energy difference matching (E_{gap+1(cat)} - E_{gap(sub)}) as a descriptor, the trend of Pd, Au and Ag shown as solid arrows (Figure 5.S4b) indicates that the electrocatalyst’s frontier or non-frontier orbital energy difference should be close and slightly larger than the electron donor’s frontier orbital energy difference to ensure the rigorous matching of energy level differences after the accelerating effects of external bias on the transferred electrons in the electrocatalytic oxidation reaction. Since formate derived from formaldehyde oxidation is very easy to be further oxidized to carbonate on Pt, the formaldehyde oxidation will involve four electrons instead of two to an extent large enough to make the frontier orbital energy difference matching insufficient to represent the whole reaction network. For glyoxylic acid and acetaldehyde oxidation on Pt, the trend is the same as Pd, Au, and Ag but not obvious since the potential window (<0.7 V vs RHE) selected for fuel cell anode application is not wide enough to include the relatively positive peak value of $TOF_{e-}$ on Pt and Pd in the whole potential range. Furthermore, as d-block transition metals, Ag and Au have more excitable d electrons in their outer shells than Pd and Pt, making them better electron traps for aldehyde oxidation.
5.1.8 References


CHAPTER 6 CONCLUSIONS

The first catalyst design strategy is increasing the catalyst's electrochemically active surface area by increasing its surface roughness and creating a 3D electrode structure. With this rationale, surface dealloyed platinum cobalt supported on carbon nanotube (SD-PtCo/CNT), 3D graphene and carbon nanotube were utilized as catalysts. By using SD-PtCo/CNT as anode catalyst and crude glycerol as fuel, high performance direct alcohol fuel cell baseline was established. An unprecedented single cell performance (268.5 mW cm$^{-2}$) and catalytic mass activity (537 mW mg$^{-1}$ per MEA) is achieved under 80 °C and ambient pressure. This performance was found to be comparable with that of SOFC operated under very high temperature (580-800 °C), filling up the blank of low temperature high performance direct glycerol fuel cell. Then, novel anode metal catalyst free and complete metal catalyst free direct carbohydrazide AEMFCs with 3D graphene (and CNT) anode catalysts have been successfully developed. Prototypes of anode metal catalyst free and completely metal catalyst free anion exchange membrane fuel cell with 3D graphene anode catalyst generate peak power density of 75.1 mW cm$^{-2}$ and 24.9 mW cm$^{-2}$, respectively. Carbon is proposed as active sites since single cell performance before and after acid treatment of anode catalysts are very close.

The second catalyst design strategy is combining different active sites which have different functions so that the reaction rate and target product yield can be improved simulataneously. For electrocatalytic oxidation of glycerol, it is found Pd can re-adsorb the desorbed glycerate in bulk electrolyte and further oxidize it to tartronate while Au can Alleviate C-C bond cleavage of C$_3$ species. Therefore, combining Pd and Au takes advantage of these effects synergistically, maximizing the yield of tartronate in electrocatalytic glycerol oxidation.
reaction. Alloyed PdAu also increases glycerol and glycerate reaction rate so that higher power output and shorter reaction time can be achieved. Electrocatalytic selective oxidation of glycerol over PdAu nanoparticle catalysts to tartronate with a high yield of 68% with cogeneration of electrical energy has been achieved in a 5 cm² AEM-DGFCs.

The third catalyst design strategy is to use a theoretical descriptor to screen and predict the catalytic activity of different active sites, followed by confirming the calculation with experiments. Orbital energy difference matching is proposed as a descriptor for electrocatalyst design and homogeneous reaction heterogenization. Combining different heterogenized active sites with well-directed high activity towards original substrate or reaction intermediates is proposed as a strategy for designing multi-functional electrocatalysts improved by spillover of reaction intermediates, which is similar to strategy 2. Taking aldehyde and alcohol oxidation as an example, the range of electrocatalyst candidates for intermediate aldehyde electro-oxidation was firstly narrowed to Lewis soft acids via HSAB theory from an adsorption aspect, followed by targeting Ag, Au and Pd with the descriptor of orbital energy difference matching from a charge transfer aspect. After experimentally confirming high electrocatalytic activity of Ag towards aldehyde oxidation, Pd with high activity towards alcohol oxidation and Ag with high activity towards aldehyde (reaction intermediate in alcohol oxidation) oxidation were combined so as to achieve the highest activity towards the entire alcohol oxidation reaction network. Direct alcohol fuel cells fed with methanol, ethanol, ethylene glycol and glycerol have been demonstrated as a potential application of PdAg/CNT as the anode catalyst.
APPENDIX PUBLICATION LIST IN PH.D. PERIOD

From 2010 to 2015[1-15]


