Direct Glycerol Fuel Cell with Polytetrafluoroethylene (PTFE) Thin Film Separator

Neeva Benipal^a, Ji Qi^a, Jacob C. Gentile^a, Wenzhen Li^{a,b,*}

^a Department of Chemical and Biological Engineering, Biorenewables Research Laboratory,
Iowa State University, Ames, IA 50011, USA

^b Ames Laboratory, USDOE, Ames, IA 50011, USA

*Corresponding Author. Tel: 01-515-294-4582, Email Address: wzli@iastate.edu (W.Li)

Abstract

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

Keywords: direct glycerol fuel cell, polytetrafluoroethylene (PTFE), thin films, porous separator, anion exchange membrane, biomass renewables

1. Introduction

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

Proton exchange membrane (PEM) based DAFCs employ high loading (e.g. > 2.0 mg cm⁻²), at both anode and cathode of precious metals such as Pt or PtRu. By comparison, anion-exchange membrane (AEM) based DAFCs have the great advantage that both the kinetics of alcohol oxidation and oxygen reduction at the anode and cathode can be greatly improved; in particular, non-noble metals, such as Fe, Co, and Ni macrocycles, can serve as cathode catalysts, significantly reducing the overall DAFC system cost [15-19]. Various studies have widely used platinum-based catalyst in low-temperature PEM-DAFCs [12, 20]. Although Pt's catalytic activity with respect to alcohols such as methanol [10], ethanol [21], glycerol [22], and ethylene glycol [23] can be very high in DAFCs, the high cost due to scarcity of Pt is problematic. Extensive efforts are therefore being carried out to design new catalysts for DAFCs and

palladium is emerging as an attractive replacement for platinum in AEM-DAFCs because it is more abundant in nature and less expensive than Pt. Unlike Pt or Pt-based electrocatalysts, Pd can be highly active for oxidation of a large variety of substrates in an alkaline environment. To prepare Pd-based electrocatalysts, intensively studies have been conducted over the past few years with the aim of increasing catalyst activity, controlling the morphology of Pd, enlarging the surface area, and improving catalyst stability [2, 24-27]. In particular, the addition of Ag to Pd/CNT significantly promotes catalytic activity for the electrooxidation of glycerol and also reduces the cost of the anode catalyst. We have recently demonstrated that a PdAg catalyst [28] can perform very well, especially in terms of current density, and has capability for cleaving C-C bonds for long-chain alcohols oxidation.

Past research studies have mainly focused on the development of designs and materials used in a fuel cell system [29-31]. A current major challenge in commercialization of fuel cell technology lies in the development of new durable membranes that will allow fuel cell operation at high temperatures without extensive humidification requirements. Traditional low-temperature fuel cells rely on ion-exchange membranes that, as the “heart of the DAFCs”, have an essential function of separating reactions at both anode and cathode, allowing only H^+ or OH^- (or other anions, such as CO_3^{2-}) to freely move across PEM or AEM, respectively. The most common AEMs require properties such as high OH^- conductivity, good chemical/thermal stability. Durability and operating stability of AEMs are becoming issues because of faster degradation at elevated temperatures and harsh conditions of alkaline electrolytes [32-35]. Choban, et al., [36] reported laminar-flow-based membraneless fuel cells. Cohen, et al., [37] also demonstrated membraneless microchannel fuel cells that utilized laminar flow in microchannels to segregate fuel and oxidant to overcome design limitations caused by the use of PEM. Hou, et al., [33]

studied a KOH-doped polybenzimidazole membrane as a polymer electrolyte membrane in direct ethanol fuel cells. It enhanced the ionic conductivity of the membrane and also decreased ethanol permeability to much less than that of Nafion membranes. Mota, et al., [38] reported use of an unconventional barrier, a polycarbonate filter paper, to separate fuel and oxidant streams in a microfluidic fuel cell. This barrier allowed diffusive transport through its pores while preventing crossover of the fuel and oxidant streams. Yang, et al., has demonstrated a peak power density of 663 mW cm^{-2} using a polymer fiber membrane (PFM) as a separator replacing the polymer electrolyte membrane in direct borohydride fuel cells. The fiber materials in the PEM are made of polypropylene, polyamide, or polyvinyl alcohol, and act as a very thin liquid electrolyte layer that allow the anions and cations, including BH_4^- , OH^- , and Na^+/K^+ , to flow across freely [39]. Cost analysis of PEM fuel cells using hydrogen or methanol as fuels has shown that the price of membranes usually contributes 8 to 10 % of the manufacturing cost of a fuel cell stack [40], but challenges still exist in the development of chemically stable ion-exchange membranes, representing a major technical obstacle hindering the commercialization of AEM-DAFCs.

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

films promises important benefits with respect to complexity, cost, and performance of the fuel cell systems.

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

2. Experimental

2.1. Chemicals

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

2.2. Synthesis of catalysts and physical characterizations

PdAg/CNT (20 wt%) was prepared via a self-developed aqueous-phase reduction method [6, 47]. Briefly, Palladium (II) nitrate dihydrate (56 mg) and silver nitrate (35.7 mg) were dissolved together in deionized water (1500 mL). Sodium citrate dihydrate (200 mg) and sodium

borohydride (40 mg) were each separately dissolved in deionized water (50 mL) and carboxyl-group functionalized multiwall carbon nanotubes (171.4 mg) were then dispersed in 100 mL of deionized water. The mixed solutions were transferred into a beaker to reduce metal precursors and in order to deposit the PdAg nanoparticles onto the surface of the CNT. The final product was washed with an additional 1 L of deionized water, collected by vacuum filtration, and dried overnight in a vacuum oven at room temperature. Pd/CNT and Ag/CNT were synthesized via a method similar to that used for PdAg/CNT. The surface morphologies of the commercial PTFE thin films were studied using a scanning electron microscope (SEM, model JEOL JSM-840A). The sample surface was coated with iridium powder under vacuum before the morphology of the PTFE thin films was investigated. The structure and morphology of the as-prepared PdAg/CNT catalysts were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD analysis of PdAg/CNT catalyst was performed on a Scintag XDS-2000 θ/θ diffractometer (Cu $K\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$)) with 35 mA filament current and 45 kV tube voltage at a continuous scan rate of 1.2 degrees per minute. The mean crystallite size of PdAg/CNT was calculated using the (220) peak based on a combination of Bragg's law and the relationship between lattice and crystal-lattice spacing given by

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

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

2.3 Half-cell tests

Half-cell tests were performed using a conventional three-electrode setup (AFCELL3, Pine Instrument), equipped with a glassy carbon working electrode (AFE3T050GC, Pine Instrument), a Hg/HgO reference electrode (MMO, CHI152, CH Instruments), and a platinum wire counter electrode (AFCTR1, Pine Instrument). All potentials in the present study were referred to MMO-(1.0 M KOH, 0.098 V vs. SHE). 2.0 mg of the as-prepared catalyst was dispersed in 1.0 mL 1-propanol by sonication to form a uniform ink. The working electrode was prepared by drop-casting 10 μL , 20 μL , and 10 μL of ink for Pd/CNT, PdAg/CNT, and Ag/CNT onto the glassy carbon electrode. 10 μL of 0.05 wt% AS-4 ionomer solution (Tokuyama, Inc) was added on top to affix the catalyst particles. Prior to testing, all the electrolytes were de-aerated by purging with high purity N_2 for 30 min at ambient temperature. Ten cycles of cyclic voltammograms (CVs) were recorded for each catalyst at a constant sweep rate of 50 mV s^{-1} in 1.0 M KOH + 0.1 glycerol.

2.4. *DGFC with PTFE thin film separator*

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

flow rate of 4.0 ml min^{-1} , while high purity O_2 was fed into the cathode compartment at a flow rate of 200 ml min^{-1} under a backpressure of 0 psig.

2.5 Durability test

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

2.6 Internal Resistance Measurements and ohmically correct cell voltage ($E_{\text{iR-free}}$)

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

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

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

3. Results & discussion

3.1 Morphology of PTFE thin film or characteristics of the PTFE thin films

Fig. 1 shows the SEM images of the surface of the three kinds of porous PTFE thin films. Pore sizes and thicknesses were provided by the manufacturer. It can be seen that there are fibrils and knots in the thin film, with enclosed micropores located among both fibers and knots. The

morphology of porous PTFE thin films usually consists of separated phases with solid nodes and fibrils due to agglomeration of the PTFE material and fine threads between the nodes [51, 52]. It can be observed that the PTFE with pore size of 0.22 μm had many small pores densely interconnected with one another, while for PTFE with 0.45 μm pore size most of the pores are lightly interconnected. However, a PTFE with pore size of 1.0 μm leaves large areas not tightly interconnected, knots not uniformly distributed, and the fibrils are weakly oriented. Fig.2 shows the MEA of PTFE thin film (a) and A901 AEM (b), and uniform catalyst layers have been obtained on both PTFE thin film and A901 membrane.

(a)

(b)

(c)

Fig.1. SEM images of different PTFE thin films (a) 0.22 μm, (b) 0.45 μm, and (c) 1.0 μm

Fig.2. Photographs of sprayed catalysts on (a) PTFE thin film and (b) A901 AEM.

3.2 *Electrocatalytic study of Pd/CNT, Ag/CNT, and PdAg/CNT in half-cell*

As demonstrated in our previous work [28], PdAg/CNT can serve as a better catalyst than Pd/CNT and Ag/CNT for electro-catalytic oxidation of glycerol in a single DGFC setup. Current density and onset potential are the two parameters used to properly evaluate the activity of the catalyst towards glycerol oxidation. Fig.3 shows the CV profiles of glycerol oxidation in N_2 saturated 1.0 M KOH + 0.1 M glycerol on Pd/CNT, PdAg/CNT, and Ag/CNT catalysts at 25°C in half-cell setting. The results show that the bimetallic PdAg/CNT catalyst exhibited higher current density (43.4 mA cm^{-2} at 0.16 V) than monometallic Pd/CNT and Ag/CNT catalysts. Furthermore, PdAg/CNT exhibited a more negative onset potential (-0.47 V) compared to those of Pd/CNT (-0.33 V), and Ag/CNT (-0.08 V). Although, Ag/CNT catalyst displayed very little to no activity toward electro-catalytic glycerol oxidation. Alloying Ag and Pd together raised the catalytic activity toward glycerol oxidation and in addition reduced the particle size from 12.9 nm (Ag/CNT) to 2.9 nm (PdAg/CNT).

Fig.3. Cyclic Voltammograms of glycerol oxidation reaction on Pd/CNT, PdAg/CNT, and Ag/CNT catalysts in 1.0 M KOH + 1.0 M glycerol, 50 mV s⁻¹, 25°C.

3.3 Effect of pore size on PTFE thin film in DGFC

To evaluate the performance of the PTFE thin film-based DGFC, three different PTFE thin films pore sizes were used to prepare MEAs. Fig. 4 displays the cell polarization and power density curves of DGFC with PTFE thin film separators using PdAg/CNT as the anode catalyst and a commercial Fe-based cathode catalyst at 80°C. The experiments were performed using three different PTFE thin film pore sizes in an aqueous solution of 6.0 M KOH + 1.0 M glycerol. The open circuit voltage (OCV) of DGFC with PTFE thin film separator with 0.22 μm pore size PTFE thin film was 0.87 V, which is 0.06 V higher than that using 0.45 μm pore size PTFE thin film, and 0.08 V higher than that using 1.0 μm pore size PTFE thin film. As the pore size of PTFE thin film increases, OCV drops due to an increase in fuel crossover from larger pores. Although glycerol can crossover from the anode through the PTFE thin film separator to the

cathode catalyst layer (CCL), the reaction of glycerol with oxygen is slow in the CCL and does not cause notable parasitic overpotential because of presence of non-Pt catalysts that are not catalytically active to glycerol oxidation at the cathode. In typical PEM-DAFCs, in addition to electrochemical reactions of alcohol oxidation on the anode and oxygen reduction on the cathode, the alcohol permeated from the anode to the cathode also reacts directly with oxygen on the cathode noble metal catalyst. The peak power density (PPD) of DGFC with PTFE thin film pore size of 1.0 μm was 129.9 mW cm^{-2} , 15.1% higher than that with PTFE thin film pore size of 0.45 μm , and 46.9% higher than that with PTFE thin film pore size of 0.22 μm . The internal resistance (IR) of DGFC with PTFE thin film with 0.22 μm pore size was 87.5 mOhm, which is 55.3% higher than that with 0.45 μm pore size PTFE thin film, and 62.9% higher than that with 1.0 μm pore size PTFE thin film. The performance improvement in the present study can be attributed to the effect of pore size of the PTFE thin film separator. In typical AEM-DAFCs, as K^+ ions do not migrate to the cathode due to only anions selectivity crossing AEM, while in DGFC with PTFE thin film separator, K^+ ions can migrate through the PTFE thin film to the cathode electrode. The PTFE thin film separator allows anions and cations, including both OH^- and K^+ , to freely cross. In this situation, it is necessary for cathode catalysts to have excellent tolerance to the poison of glycerol and good stability in high alkaline solution. The cathode catalyst is a Fe-based macrocycle catalysts (ACTA 4020), used in this study has been proven to be stable enough in alkaline solution, in terms the cathode Fe-based catalyst does not surface-poisoned by K^+ and glycerol. It is known that strong adsorbed anions, such as SO_4^{2-} , HSO_4^- , can chemically adsorbed on noble metal surface (e.g., Pt and Pd) and decrease its electrocatalytic activity. Cations, such as Na^+ , K^+ will not chemical adsorbed on the noble metal surface to influence glycerol electro-oxidation reaction. Indeed, with the base concentration increasing (to

some extent), the glycerol electro-oxidation activity increases, it is mainly due to the protonation of glycerol relies on OH^- , it is called base catalysis [53], while from the other point of view, the increasing of cations (K^+ or Na^+) with base concentration increasing does not counter its activity enhancement. The traditional role of an AEM is to provide a conductive path for the OH^- ion migration and to prevent the crossover. While crossover of the fuel to the cathode is a general issue, proper modification of MEA can provide the solution to the crossover problem. In addition, the hydrophilic nature of the PTFE separator provides a smaller hydraulic liquid pressure in the cathode, enabling a reduction in water crossover and hence alleviation of cell performance. In summary, the large pore size of PTFE thin film ($1.0\text{ }\mu\text{m}$) enhances diffusion of the charge carriers (OH^-) transport process to maximize the fuel cell performance.

3.4 *Effect of PTFE thin film thickness in DGFC*

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

Fig.4. Polarization and power density curves of DGFC for different pore sizes of PTFE thin films (0.22, 0.45, 1.0 μm). Anode: PdAg/CNT (20 wt%), 1.0 $\text{mg}_{\text{pdag}} \text{cm}^{-2}$, 6.0M KOH + 1.0 M glycerol, 4.0 ml min^{-1} . Cathode: 4020 Acta, 3.0 mg cm^{-2} , O_2 , 200 sccm; ambient pressure

3.5 Effect of temperature on PTFE thin film in DGFC

Fig. 5 shows the cell polarization and power density curves of DGFC with 1.0 μm pore size PTFE thin film operated at different temperatures. It can be observed that cell performance increases with operating temperatures. An increase in temperature enhances the electrochemical kinetics of both glycerol oxidation reactions at the anode and oxygen reduction reaction (ORR) at the cathode. The OCVs of DGFC operating at 25, 40, 60 and 80°C were 0.65, 0.68, 0.74, and 0.79V, while the PPDs were 18.4, 42.8, 83.9, and 129.9 mW cm^{-2} , respectively. The conductivity of the hydroxyl ions increases with increasing temperature, reducing the ohmic loss. It is obvious that cell resistance is decreased as the temperature is increased and as a result the cell performance is improved. A higher temperature improves the glycerol oxidation kinetics, leading to higher fuel cell output power density. Furthermore, both glycerol and oxygen transport diffusivities are increased with an increase in temperature, resulting in low mass transport

polarization. PTFE thin films have proven to have excellent endurance in alkaline media and are chemically/thermally stable [55]. The cell performance increases as the temperature is increased; this can be attributed to the faster electrochemical kinetics and increased conductivity of hydroxyl ions and of reactant and products.

Fig.5. Polarization and power density curves of DGFC at different temperatures. Anode: PdAg/CNT (20 wt%), $1.0 \text{ mg}_{\text{pdag}} \text{ cm}^{-2}$, 6.0 M KOH + 1.0 M glycerol, 4.0 ml min^{-1} . Cathode: 4020 Acta, 3.0 mg cm^{-2} , O_2 , 200 sccm, ambient pressure.

3.6 Performance comparison of AEM and PTFE thin film in DGFCs

The performances of DGFC employing the PTFE thin film (pore size: $0.45 \mu\text{m}$, thickness $215 \mu\text{m}$) and A901 AEM (no pore, thickness: $10 \mu\text{m}$) under optimized conditions were investigated. In our earlier work [6, 22], various concentrations of KOH and anode fuel were investigated, and it was found that 6.0 M KOH + 3.0 M fuel concentration produced the highest peak power density [6]. Therefore, in subsequent experiments 6.0 M KOH + 3.0 M glycerol was selected as the optimal fuel. Fig.6 illustrates the cell polarization and power density curves of

DGFCs with PTFE thin film and A901 AEM using PdAg/CNT as the anode catalyst at 80°C. It can be observed that the OCV of porous PTFE thin film-DGFC is 0.88 V, which is 0.02 V higher than that for A901 AEM. Our previous pore size effect test has demonstrated that the pore size distribution of the thin film is a critical parameter for maximizing fuel cell performance because of its effect on the transport process diffusion of charge carriers (OH⁻). The internal resistance of A901 AEM in DGFC was 11.5 mOhm, which is half of that when using porous PTFE thin films. It can be clearly observed that, as the internal resistance is decreased, cell performance is improved. The PPD of DGFC with A901 AEM is 277.7 mW cm⁻² which is 22.6% higher than the PPD of the porous PTFE thin film (0.45 μm). The practical ohmic losses are due to both electronic contact resistance between the flow fields and the diffusion media as well as the ohmic resistance due to hydroxyl ions conducting through the membrane or the substrate [56]. Therefore, the ohmically-corrected cell voltage, $E_{iR-free}$, can be determined directly from the experimental data.

The IR-free corrected curves for DGFC with PTFE thin film separator and Anion-exchange membrane were plotted using Equation [1], as shown in Fig. 7. The factors contributing to the ohmic losses are the membrane's ionic conductivity, the membrane thickness (10 μm vs. 215 μm), the electrolyte conductivity, and the catalyst resistance layer. It is clearly noticeable that cell performance of DGFC with PTFE thin film and AEM based DGFC has significantly improved by reducing the ohmic loss. This should guide the future design of PTFE thin film separators to be small in resistance, so as to generate higher fuel cell power density. Furthermore, while modifying and developing the porous PTFE thin films could demonstrate the feasibility of replacing the large-scale ion-exchange membranes. However, the anticipated drawbacks of using PTFE thin films are that fuel and oxidant species would undesirably be

affected by allowing cross reactions. Choosing more appropriate catalysts can be an alternative approach to this problem. In our system, Fe-based cathode catalyst (4020 Acta) has relatively mild catalytic activity towards glycerol oxidation during crossover.

Fig.6. Polarization and power density curves of DGFC with A901 AEM and PTFE thin film ($0.45 \mu\text{m}$). Anode: PdAg/CNT, $1.0 \text{ mg}_{\text{pdag}} \text{ cm}^{-2}$, $6.0 \text{ M KOH} + 3.0 \text{ M glycerol}$; 4.0 ml min^{-1} . Cathode: 4020 Acta, 3.0 mg cm^{-2} , O_2 , 200 sccm , 80°C .

Fig.7. Polarization and power density curves of DGFC with iR-corrected for PTFE thin film. Anode: PdAg/CNT, $1.0 \text{ mg}_{\text{pdag}} \text{ cm}^{-2}$, 6.0 M KOH + 3.0 M glycerol; 4.0 ml min^{-1} . Cathode: 4020 Acta, 3.0 mg cm^{-2} , O_2 , 200 sccm, 80°C .

3.7 Primary Cost Analysis

The cost of noble metal catalysts and membranes is the main factor for limiting fuel cell commercialization. The cost of the porous PTFE thin films used in our work is $\sim \$8.06 \text{ m}^{-2}$. Commercially available anion-exchange membranes (A901) had a cost of $\sim \$992.1 \text{ m}^{-2}$ (based on small quantity manufacturing cost). Supposing that a $6 \times 7 \text{ cm}$ area per MEA is needed, PTFE thin film would cost $\sim \$0.04$ per MEA, obviously much less than an A901 AEM that costs $\sim \$4.31$ per MEA. An estimate based on the price of PTFE thin films and AEMs shows that PTFE thin films cost substantially less when compared with A901 AEMs. It should be noted that economy of scale may bring about a cost reduction in the anion exchange membrane Tokuyama

A901. From a fuel cell technology viewpoint, an essential development strategy would be to reduce the costs of fuel cell components. Furthermore, techno-economic analysis could provide economic indicators for use of future alternative PTFE thin films in fuel cell technologies.

3.8 *Cell voltage degradation for AEM and PTFE thin film in DGFCs*

A durability test was used to evaluate the endurance of PTFE thin films and A901 AEMs for DGFC. Fig.8 shows results from the 80 h durability test of DGFC with A901 AEM and PTFE thin film at a constant density of 50 mA cm^{-2} at 80°C . It is interesting to observe that the initial voltage for a PTFE thin film DGFC is about 110 mV higher than that for an AEM-DGFC (0.61 V vs. 0.50 V), suggesting that the steady-state operational performance of PTFE thin film DGFC is better than that of AEM-DGFC. It can be observed that the absolute voltage of both the A901 AEM and the PTFE thin film dropped remarkably after an operational time of about 80 h. The cell voltage decreased with the discharge time, i.e., a 5.8% drop for PTFE thin film and 11.1% drop in cell voltage for A901 AEM over a test period of 80 h. Similarly, the degradation rate of the cell voltage decreased from 1.2 mV h^{-1} to 0.8 mV h^{-1} for PTFE thin film, and for the A901 AEM from 9.6 mV h^{-1} to 3.0 mV h^{-1} over the 80 h period. The cell voltage decreased with time but was partially recovered after each interruption (20, 40, 60, and 80 h), caused by the stop/restart procedure. Such fuel cell degradation can be either reversible or irreversible degradations [57]. The possible voltage that could be recovered by the stop/restart procedure was defined to be reversible degradation, while, the voltage that could not be recovered by the stop/restart procedure was defined to be irreversible degradation [58]. The irreversible degradation loss might be triggered by a change in the microstructure of the catalyst due to agglomeration, dissolution of catalysts, or inactivity of active sites due to fuel crossover. The origin of reversible degradation loss is due to elimination of the hydrophobic property of gas

diffusion layer used on the cathode electrode that results in flooding of MEA; this could be alleviated by changing the airflow rate. KOH in the fuel solution enhances the ionic conductivity of the membrane, producing in the porous PTFE thin film the features of an alkali-doped polymer membrane [18]. The drop in cell voltage and degradation rate percentage is much higher for DGFC with A901 AEM than for PTFE thin film. This demonstrates that PTFE thin films have better endurance than A901 AEM in DGFCs.

Fig.8. Transient cell voltage curves at constant current density of 50 mA cm^{-2} over 80 h period of DGFC. Anode: PdAg/CNT, $1.0 \text{ mg}_{\text{pdag}} \text{ cm}^{-2}$, 6.0 M KOH + 1.0 M glycerol, 1.0 ml min^{-1} . Cathode: 4020 Acta, 3.0 mg cm^{-2} , O_2 , 100 sccm, ambient pressure, 80°C .

3.9 Electrode degradation on anode

Fig.9 shows the TEM images and the corresponding metal particle size histograms of PdAg particles supported on CNT both before and after the durability test. The bimetallic PdAg nanoparticles are well dispersed on CNT with uniform particle size distribution. The average

particle size, determined by randomly measuring 100 particles, was 2.9 nm. The particle size distributions are fairly narrow, ranging from 2.2 to 3.8 nm for PdAg before the durability test and 2.4 to 5.0 nm for PdAg after the durability test. The TEM results show that the average particle size of the anode catalyst increases from 2.9 nm to 3.7 nm after the durability test, reducing the electrochemically active surface area and hence causing a decrease in anode performance. A small amount of agglomerations of PdAg particles appear on the CNT support while individual PdAg particles have also grown, broadening the average particle size to 3.7 nm. The growth caused by the random cluster-cluster collisions accompanied by liquid-like coalescence of the particles may contribute to the agglomeration and growth of the catalyst particles [59]. XRD patterns for PdAg/CNT catalyst before and after the durability test are shown in Fig. 10. The peak of 25° , which is the wide graphite (002) peak, suggests that CNT support has a good graphite characteristic. It can be observed that there is no further peak shift (111, 200, 220, and 311) of PdAg/CNT before and after the durability test. The mean crystal size values calculated using the Debye-Scherrer formula were 2.9 nm and 3.6 nm, respectively, for PdAg/CNT before and after the durability test, in good agreement with the TEM results. It could therefore be logically concluded that PdAg/CNT remains alloyed and crystalline after the 80 h durability interval. We proposed that the decrease in the cell voltage after long-term discharge is mainly attributable to the loss of the anode performance.

Fig.9. TEM images of PdAg/CNT before (a) and after (b) the durability test.

Fig.10. XRD image of PdAg/CNT before and after the durability test.

3.10 Future outlook

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

4. Conclusions

In the present work, DGFC was developed using a porous PTFE thin film as a separator of fuel and oxidant streams. The electrocatalytic activities of Pd/CNT, PdAg/CNT, and Ag/CNT on glycerol oxidation, identified by cyclic voltammetry, showed that PdAg/CNT produces the highest current density. DGFCs using PTFE thin film with PdAg/CNT anode catalyst and Fe-based cathode catalyst achieved a maximum peak power density of 214.7 mW cm^{-2} at 80°C . Three porous PTFE films of different pore sizes and thicknesses were studied to seek understanding of the link between pore size and cell performance. The pore size effect of PTFE thin film separator showed that a larger thin film pore size of $1.0 \text{ }\mu\text{m}$ enhanced diffusion in the charge carriers (OH^-) transport process to maximize fuel cell performance. The performance of DGFCs employed with PTFE thin film and A901 AEM was investigated for comparison. Although the real performance of the DGFC employed with PTFE thin film is 22.6% lower than that of A901 AEM-based DGFC, IR-corrected polarization curves of the PTFE thin film DGFC suggest that fuel cell performances are indeed very close after removing internal resistance. Considering the thickness, PTFE thin film ($215 \text{ }\mu\text{m}$) raises twice internal resistance than A901 AEM ($10 \text{ }\mu\text{m}$), future PTFE thin film research should be focused on optimizing thickness, pore structure, and hydrophobicity to reduce fuel cell's internal resistance, thus improving the overall fuel cell performance. The 80 h durability test indicated that the major voltage loss occurs during the initial discharge stage, but the loss becomes smaller and more stable with discharge time. We report a 5.8% decrease in cell voltage for PTFE thin film DGFC and an 11.1% decrease in cell voltage for A901 AEM-DGFC; the degradation rate of cell voltage over the 80 h period similarly decreases from 1.2 mV h^{-1} to 0.8 mV h^{-1} for PTFE thin film, and for A901 AEM from 9.6 mV h^{-1} to 3.0 mV h^{-1} . The voltage loss is mainly caused by performance reduction at the anode due to

both the agglomeration and the growth of the catalyst particles from 2.9 to 3.7 nm. Using DGFCs with PTFE thin films separator without further synthesizing or modification, these films in this work breaks the paradigm and demonstrates a PTFE thin film separator capable of operating with lower ionic resistance than benchmark state-of-the-art anion exchange membranes.

Acknowledgements

We acknowledge financial support from the US National Science Foundation (CBET-1512126) and the Iowa State University startup fund. The authors are grateful to Darcie H. Farrell and Qi Liu of Iowa State University for assistance in fuel cell experiments.

References:

- [1] J. Zhang, S. Lu, Y. Xiang, P.K. Shen, J. Liu, S.P. Jiang, Carbon-Nanotubes-Supported Pd Nanoparticles for Alcohol Oxidations in Fuel Cells: Effect of Number of Nanotube Walls on Activity, *ChemSusChem* 8(17) (2015) 2956-2966.
- [2] A.A. Daryakenari, D. Hosseini, T. Saito, A. Apostoluk, C.R. Muller, J.-J. Delaunay, Ethanol electro-oxidation on nanoworm-shaped Pd particles supported by nanographitic layers fabricated by electrophoretic deposition, *RSC Advances* 5(65) (2015) 52578-52587.
- [3] X. Li, *Principles of Fuel Cells* Taylor & Francis Group, LLC (2006).
- [4] K. Matsuoka, Y. Iriyama, T. Abe, M. Matsuoka, Z. Ogumi, Alkaline direct alcohol fuel cells using an anion exchange membrane, *Journal of Power Sources* 150(0) (2005) 27-31.
- [5] Y.S. Li, T.S. Zhao, Z.X. Liang, Performance of alkaline electrolyte-membrane-based direct ethanol fuel cells, *Journal of Power Sources* 187(2) (2009) 387-392.
- [6] J. Qi, L. Xin, Z. Zhang, K. Sun, H. He, F. Wang, D. Chadderdon, Y. Qiu, C. Liang, W. Li, Surface dealloyed PtCo nanoparticles supported on carbon nanotube: facile synthesis and promising application for anion exchange membrane direct crude glycerol fuel cell, *Green Chemistry* 15(5) (2013) 1133-1137.
- [7] Z. Zhang, L. Xin, W. Li, Electrocatalytic oxidation of glycerol on Pt/C in anion-exchange membrane fuel cell: Cogeneration of electricity and valuable chemicals, *Applied Catalysis B: Environmental* 119-120 (2012) 40-48.
- [8] A. Kirubakaran, S. Jain, R.K. Nema, A review on fuel cell technologies and power electronic interface, *Renewable and Sustainable Energy Reviews* 13(9) (2009) 2430-2440.
- [9] C. Lamy*, C. Coutanceau, Chapter 1 Electrocatalysis of Alcohol Oxidation Reactions at Platinum Group Metals, *Catalysts for Alcohol-Fuelled Direct Oxidation Fuel Cells*, The Royal Society of Chemistry 2012, pp. 1-70.
- [10] A.N. Lai, K. Zhou, Y.Z. Zhuo, Q.G. Zhang, A.M. Zhu, M.L. Ye, Q.L. Liu, Anion exchange membranes based on carbazole-containing polyolefin for direct methanol fuel cells, *Journal of Membrane Science* 497 (2016) 99-107.

- [11] A. Alipour Najmi, S. Rowshanzamir, M.J. Parnian, Investigation of NaOH concentration effect in injected fuel on the performance of passive direct methanol alkaline fuel cell with modified cation exchange membrane, *Energy* 94 (2016) 589-599.
- [12] P. Joghee, J.N. Malik, S. Pylypenko, R. O'Hayre, A review on direct methanol fuel cells – In the perspective of energy and sustainability, *MRS Energy & Sustainability - A Review Journal* 2 (2015) E3 (31 pages).
- [13] S.Y. Shen, T.S. Zhao, Q.X. Wu, Product analysis of the ethanol oxidation reaction on palladium-based catalysts in an anion-exchange membrane fuel cell environment, *International Journal of Hydrogen Energy* 37(1) (2012) 575-582.
- [14] Z. Zhang, L. Xin, K. Sun, W. Li, Pd–Ni electrocatalysts for efficient ethanol oxidation reaction in alkaline electrolyte, *International Journal of Hydrogen Energy* 36(20) (2011) 12686-12697.
- [15] S.R. Narayanan, T. Valdez, N. Rohatgi, W. Chun, G. Hoover, G. Halpert, Recent advances in direct methanol fuel cells, *Battery Conference on Applications and Advances*, 1999. The Fourteenth Annual, 1999, pp. 73-77.
- [16] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, Recent advances in direct methanol fuel cells at Los Alamos National Laboratory, *Journal of Power Sources* 86(1–2) (2000) 111-116.
- [17] J.S. Spendelow, A. Wieckowski, Electrocatalysis of oxygen reduction and small alcohol oxidation in alkaline media, *Physical Chemistry Chemical Physics* 9(21) (2007) 2654-2675.
- [18] T. Zhao, Y. Li, S. Shen, Anion-exchange membrane direct ethanol fuel cells: Status and perspective, *Frontiers of Energy and Power Engineering in China* 4(4) (2010) 443-458.
- [19] W.J. Zhou, S.Q. Song, W.Z. Li, G.Q. Sun, Q. Xin, S. Kontou, K. Pouliaitis, P. Tsiakaras, Pt-based anode catalysts for direct ethanol fuel cells, *Solid State Ionics* 175(1–4) (2004) 797-803.
- [20] L. An, T.S. Zhao, Y.S. Li, Carbon-neutral sustainable energy technology: Direct ethanol fuel cells, *Renewable and Sustainable Energy Reviews* 50 (2015) 1462-1468.
- [21] S.P.S. Badwal, S. Giddey, A. Kulkarni, J. Goel, S. Basu, Direct ethanol fuel cells for transport and stationary applications – A comprehensive review, *Applied Energy* 145 (2015) 80-103.
- [22] Z. Zhang, L. Xin, J. Qi, D.J. Chadderton, W. Li, Supported Pt, Pd and Au nanoparticle anode catalysts for anion-exchange membrane fuel cells with glycerol and crude glycerol fuels, *Applied Catalysis B: Environmental* 136–137 (2013) 29-39.
- [23] L. Xin, Z. Zhang, J. Qi, D. Chadderton, W. Li, Electrocatalytic oxidation of ethylene glycol (EG) on supported Pt and Au catalysts in alkaline media: Reaction pathway investigation in three-electrode cell and fuel cell reactors, *Applied Catalysis B: Environmental* 125 (2012) 85-94.
- [24] S. Dash, N. Munichandraiah, Electrocatalytic oxidation of C3-aliphatic alcohols on electrodeposited Pd-PEDOT nanodendrites in alkaline medium, *Journal of The Electrochemical Society* 160(4) (2013) H197-H202.
- [25] G. Hu, F. Nitze, X. Jia, T. Sharifi, H.R. Barzegar, E. Gracia-Espino, T. Wågberg, Reduction free room temperature synthesis of a durable and efficient Pd/ordered mesoporous carbon composite electrocatalyst for alkaline direct alcohols fuel cell, *Rsc Advances* 4(2) (2014) 676-682.
- [26] A.-L. Wang, H. Xu, J.-X. Feng, L.-X. Ding, Y.-X. Tong, G.-R. Li, Design of Pd/PANI/Pd Sandwich-Structured Nanotube Array Catalysts with Special Shape Effects and Synergistic Effects for Ethanol Electrooxidation, *Journal of the American Chemical Society* 135(29) (2013) 10703-10709.
- [27] C. Zhang, J. Sun, J. Xu, X. Wang, H. Ji, C. Zhao, Z. Zhang, Formation and microstructure of nanoporous silver by dealloying rapidly solidified Zn–Ag alloys, *Electrochimica Acta* 63 (2012) 302-311.
- [28] J. Qi, N. Benipal, C. Liang, W. Li, PdAg/CNT catalyzed alcohol oxidation reaction for high-performance anion exchange membrane direct alcohol fuel cell (alcohol = methanol, ethanol, ethylene glycol and glycerol), *Applied Catalysis B: Environmental* 199 (2016) 494-503.

- [29] Y.S. Li, T.S. Zhao, J.B. Xu, S.Y. Shen, W.W. Yang, Effect of cathode micro-porous layer on performance of anion-exchange membrane direct ethanol fuel cells, *Journal of Power Sources* 196(4) (2011) 1802-1807.
- [30] J.R. Varcoe, P. Atanassov, D.R. Dekel, A.M. Herring, M.A. Hickner, P.A. Kohl, A.R. Kucernak, W.E. Mustain, K. Nijmeijer, K. Scott, T. Xu, L. Zhuang, Anion-exchange membranes in electrochemical energy systems, *Energy & Environmental Science* 7(10) (2014) 3135-3191.
- [31] Q. Yi, Q. Chen, Z. Yang, A novel membrane-less direct alcohol fuel cell, *Journal of Power Sources* 298 (2015) 171-176.
- [32] D. Chen, M.A. Hickner, Degradation of Imidazolium- and Quaternary Ammonium-Functionalized Poly(fluorenyl ether ketone sulfone) Anion Exchange Membranes, *ACS Applied Materials & Interfaces* 4(11) (2012) 5775-5781.
- [33] H. Hou, S. Wang, Q. Jiang, W. Jin, L. Jiang, G. Sun, Durability study of KOH doped polybenzimidazole membrane for air-breathing alkaline direct ethanol fuel cell, *Journal of Power Sources* 196(6) (2011) 3244-3248.
- [34] V. Neagu, I. Bunia, I. Plesca, Ionic polymers VI. Chemical stability of strong base anion exchangers in aggressive media, *Polymer Degradation and Stability* 70(3) (2000) 463-468.
- [35] Y. Yang, J. Loomis, H. Ghasemi, S.W. Lee, Y.J. Wang, Y. Cui, G. Chen, Membrane-Free Battery for Harvesting Low-Grade Thermal Energy, *Nano Letters* 14(11) (2014) 6578-6583.
- [36] E.R. Choban, J. Spendelow, L. Gancs, A. Wieckowski, P. Kenis, Membraneless laminar flow-based micro fuel cells operating in alkaline, acidic, and acidic/alkaline media, *Electrochimica Acta* 50(27) (2005) 5390-5398.
- [37] J.L. Cohen, D.J. Volpe, D.A. Westly, A. Pechenik, H.D. Abruña, A Dual Electrolyte H₂/O₂ Planar Membraneless Microchannel Fuel Cell System with Open Circuit Potentials in Excess of 1.4 V, *Langmuir* 21(8) (2005) 3544-3550.
- [38] N.D. Mota, D.A. Finkelstein, J.D. Kirtland, C.A. Rodriguez, A.D. Stroock, H.D. Abruña, Membraneless, Room-Temperature, Direct Borohydride/Cerium Fuel Cell with Power Density of Over 0.25 W/cm², *Journal of the American Chemical Society* 134(14) (2012) 6076-6079.
- [39] X. Yang, Y. Liu, S. Li, X. Wei, L. Wang, Y. Chen, A direct borohydride fuel cell with a polymer fiber membrane and non-noble metal catalysts, *Scientific Reports* 2 (2012) 567.
- [40] Y. Yang, Portable Power Fuel Cell Manufacturing Cost Analyses, Austin Power Engineering LLC, Austin Power Engineering LLC, San Antonio, TX, 2010.
- [41] Y.S. Li, T.S. Zhao, A high-performance integrated electrode for anion-exchange membrane direct ethanol fuel cells, *International Journal of Hydrogen Energy* 36(13) (2011) 7707-7713.
- [42] G.K.S. Prakash, F.C. Krause, F.A. Viva, S.R. Narayanan, G.A. Olah, Study of operating conditions and cell design on the performance of alkaline anion exchange membrane based direct methanol fuel cells, *Journal of Power Sources* 196(19) (2011) 7967-7972.
- [43] X. Yang, Y. Liu, Y. Fang, L. Wang, S. Li, X. Wei, A direct methanol fuel cell without the use of a polymer electrolyte membrane or precious metal cathode catalyst, *Journal of Power Sources* 234 (2013) 272-276.
- [44] H.-L. Lin, T.L. Yu, L.-N. Huang, L.-C. Chen, K.-S. Shen, G.-B. Jung, Nafion/PTFE composite membranes for direct methanol fuel cell applications, *Journal of Power Sources* 150 (2005) 11-19.
- [45] F. Liu, B. Yi, D. Xing, J. Yu, H. Zhang, Nafion/PTFE composite membranes for fuel cell applications, *Journal of Membrane Science* 212(1-2) (2003) 213-223.
- [46] T.L. Yu, H.-L. Lin, K.-S. Shen, L.-N. Huang, Y.-C. Chang, G.-B. Jung, J. Huang, Nafion/PTFE Composite Membranes for Fuel Cell Applications, *Journal of Polymer Research* 11(3) (2004) 217-224.
- [47] J. Qi, L. Xin, D.J. Chadderton, Y. Qiu, Y. Jiang, N. Benipal, C. Liang, W. Li, Electrocatalytic selective oxidation of glycerol to tartronate on Au/C anode catalysts in anion exchange membrane fuel cells with electricity cogeneration, *Applied Catalysis B: Environmental* 154-155 (2014) 360-368.

- [48] J. Qi, N. Benipal, D.J. Chadderdon, J. Huo, Y. Jiang, Y. Qiu, X. Han, Y.H. Hu, B.H. Shanks, W. Li, Carbon nanotubes as catalysts for direct carbohydrazide fuel cells, *Carbon* 89(0) (2015) 142-147.
- [49] J. Qi, N. Benipal, H. Wang, D.J. Chadderdon, Y. Jiang, W. Wei, Y.H. Hu, W. Li, Back Cover: Metal-Catalyst-Free Carbohydrazide Fuel Cells with Three-Dimensional Graphene Anodes (*ChemSusChem* 7/2015), *ChemSusChem* 8(7) (2015) 1288-1288.
- [50] L. Xin, Z. Zhang, Z. Wang, W. Li, Simultaneous Generation of Mesoxalic Acid and Electricity from Glycerol on a Gold Anode Catalyst in Anion-Exchange Membrane Fuel Cells, *ChemCatChem* 4(8) (2012) 1105-1114.
- [51] M. Wegener, W. Wirges, B. Tiersch, Porous polytetrafluoroethylene (PTFE) electret films: porosity and time dependent charging behavior of the free surface, *Journal of Porous Materials* 14(1) (2006) 111-118.
- [52] X. Zhongfu, G.-M. Reimund, K. Wolfgang, W. Armin, D. Rudi, High surface-charge stability of porous polytetrafluoroethylene electret films at room and elevated temperatures, *Journal of Physics D: Applied Physics* 32(17) (1999) L83.
- [53] K.J.P. Schouten, Z. Qin, E.P. Gallent, M.T.M. Koper, Two Pathways for the Formation of Ethylene in CO Reduction on Single-Crystal Copper Electrodes, *Journal of the American Chemical Society* 134(24) (2012) 9864-9867.
- [54] W. Sung, J.-W. Choi, A membraneless microscale fuel cell using non-noble catalysts in alkaline solution, *Journal of Power Sources* 172(1) (2007) 198-208.
- [55] Y. Zhao, H. Yu, D. Xing, W. Lu, Z. Shao, B. Yi, Preparation and characterization of PTFE based composite anion exchange membranes for alkaline fuel cells, *Journal of Membrane Science* 421-422 (2012) 311-317.
- [56] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, *Applied Catalysis B: Environmental* 56(1-2) (2005) 9-35.
- [57] H.-C. Cha, C.-Y. Chen, J.-Y. Shiu, Investigation on the durability of direct methanol fuel cells, *Journal of Power Sources* 192(2) (2009) 451-456.
- [58] S. Kundu, M. Fowler, L.C. Simon, R. Abouatallah, Reversible and irreversible degradation in fuel cells during Open Circuit Voltage durability testing, *Journal of Power Sources* 182(1) (2008) 254-258.
- [59] J. Wu, X.Z. Yuan, J.J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, W. Merida, A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies, *Journal of Power Sources* 184(1) (2008) 104-119.
- [60] S. Gu, R. Cai, T. Luo, K. Jensen, C. Contreras, Y. Yan, Quaternary Phosphonium-Based Polymers as Hydroxide Exchange Membranes, *ChemSusChem* 3(5) (2010) 555-558.
- [61] R.C. Weast, *CRC Handbook of Chemistry, and Physics*, 70th ed., CRC Press, Boca Raton, FL, 1989.

Graphical Abstract:

Direct Glycerol Fuel Cell with PTFE Thin Film Separator