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Two Dimensional Point of Use Fuel Cell – a Final LDRD Project Report

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Abstract

The Proliferation Assessment (program area - Things Thin) within the Defense Systems and Assessment Investment Area desires high energy density and long-lived power sources with moderate currents (mA) that can be used as building blocks in platforms for the continuous monitoring of chemical, biological, and radiological agents. Fuel cells can be an optimum choice for a power source because of the high energy densities that are possible with liquid fuels. Additionally, power generation and fuel storage can be decoupled in a fuel cell for independent control of energy and power density for customized, application-driven power solutions. Direct methanol fuel cells (DMFC) are explored as a possible concept to develop into ultrathin or two-dimensional power sources. New developments in nanotechnology, advanced fabrication techniques, and materials science are exploited to create a planar DMFC that could be co-located with electronics in a chip format. Carbon nanotubes and pyrolyzed polymers are used as building block electrodes - porous, mechanically compliant current collectors. Directed assembly methods including surface functionalization and layer-by-layer deposition with polyelectrolytes are used to pattern, build, and add functionality to these electrodes. These same techniques are used to incorporate nanoscale selective electrocatalyst into the carbon electrodes to provide a high density of active electron transfer sites for the methanol oxidation and oxygen reduction reactions. The resulting electrodes are characterized in terms of their physical properties, electrocatalytic function, and selectivity to better understand how processing impacts their performance attributes. The basic function of a membrane electrode assembly is demonstrated for several prototype devices.

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1.0 Introduction

The Proliferation Assessment (program area - Things Thin) within the Defense Systems and Assessment Investment Area desires high energy density and long-lived power sources with moderate currents (mA) that can be used as building blocks in platforms for the continuous monitoring of chemical, biological, and radiological agents. Fuel cells can be an optimum choice for a power source because of the high energy densities that are possible with liquid fuels. Additionally, power generation and fuel storage can be decoupled for independent control of energy and power density for customized, application-driven power solutions. As a point of comparison, the specific and volumetric energy densities for commercial rechargeable Li ion and primary Zn-air batteries are compared to that of a direct methanol fuel cell (DMFC) in Table 1.

Table 1. Comparison of the Energy Density and Operational Temperature Range for Commercial Li Ion and Zn-Air Batteries versus a DMFC.

Source	Energy Density		Temperature Range (°C)	
	Whkg ⁻¹	WhL ⁻¹	Min	Max
Li ion	200	530	> -40	60
Zn:Air	220	250	-10	55
DMFC	300	1000	4	60

The DMFC is assumed to be operating at 20% of the theoretical energy density for this comparison. The benefit of a liquid electrochemical fuel is higher energy density, although the use of an aqueous electrolyte limits the lower operational temperature.

Fuel cells are electrochemical reactors that convert a fuel like methanol and an oxidant like oxygen into carbon dioxide and water while releasing 6 electrons at a finite potential. The chemical reaction written for an acidic environment is as follows:

This reaction occurs with near equal efficiency in alkaline media although variations exist in electrocatalysts used to drive the two half reactions. A mixed reactant fuel cell eliminates the need for separate fuel and oxidant supply manifolds and utilizes electrocatalysts that are immune to reactant cross-over.¹ A passive fuel cell is considered a source where fuel and oxidant are supplied at ambient pressures, without the aid of forced flow. Miniaturizing a fuel cell to form a low- or two-dimensional power source would be more readily accomplished using a mixed reactant, passive approach.

The concept of ultrathin or two-dimensional fuel cells is not a new idea. Barton et al. explored mixed reactant (fuel and oxidant) designs based on bi-polar electrodes and selective electrocatalysts.² The term selective indicates an MOR or ORR electrocatalyst that are tolerant of the presence of O₂ and CH₃OH, respectively. Analysis of this strip cell design indicated that relatively large (> 100 μm) out-of-plane thickness was required for efficient operation.

Additionally, the test cells used commercial membrane electrode assemblies and electrocatalysts, as emphasis was not placed on low dimensional materials and structures for integration into an ultrathin form factor, such as personal electronic devices. Mitrovski and Nuzzo explored microelectronic fabrication of a passive, microfluidic hydrogen-air fuel cell.³ Where the use of hydrogen as a fuel is attractive from the perspective of power output and stability, methanol is a far better fuel when considering energy density and simplicity of the power source. More recently, Lam et al. have demonstrated a single support electrode DMFC that forms an anode:separator:cathode stack cell.⁴ This device was created by spray depositing first a cellulose acetate film onto a carbon fiber paper with anode catalyst, followed by spray deposition of a cathode electrocatalyst ink. The final thickness of this cell was 390 μm . The goal was to enhance power density and minimize ohmic losses with this design. Successful miniaturization to produce two-dimensional fuel cells will require the application of novel materials for more than just the separator (cellulose acetate in this case) and new methods for the integration of these materials to make better use of limited vertical dimensions.

The work described within this report takes advantage of recent developments in nanotechnology, advanced fabrication techniques, and materials science to reduce required length scales to levels that enable the fabrication of a two-dimensional fuel cell. Carbon nanotubes and pyrolyzed polymers are as the building block, porous, mechanically compliant current collectors. Directed assembly methods including surface functionalization and layer-by-layer deposition with polyelectrolytes are used to pattern and build these electrodes. These same techniques are used to incorporate nanoscale selective electrocatalyst into the carbon electrodes to provide a high density of active electron transfer sites for the MOR and ORR reactions. The resulting electrodes are characterized in terms of their physical properties, electrocatalytic function, and selectivity to better understand how processing impacts attributes. The basic function of a membrane electrode assembly is demonstrated for several prototype devices. Further work will be needed to realize a fully functional, stable two-dimensional fuel cell.

2. Two Dimensional Strip Cell

Carbon nanotubes (CNTs) appear as particularly attractive building blocks for fabricating carbon electrodes as current collectors for miniaturized power source applications. The combination of high electrical conductivity (for armchair and zigzag conformations),⁵ size/shape, and available surface chemistry allows for compact, porous, and physically scalable structures to be produced using relatively simple solution-based processing. Two examples of CNT-based electrode fabrication were explored as part of this study: 1) patterned chemical functionalization of a surface followed by solution-based, electrostatically driven self-assembly and 2) filtration-derived mats cut and transferred to a solid support substrate.

2.1 Patterned Electrode Fabrication

Patterned CNT electrode arrays were fabricated on Si using a layer-by-layer (LbL) assembly process. The LbL process is a solution-based self assembly technique where polyelectrolytes, separate anionic and a cationic components, are used sequentially to “build up” a film comprised

of the individual layers.⁶ LbL has been previously demonstrated as a method for generating CNT:polymer composite films.⁷ The process used in this current study is shown in Figure 1.

Figure 1. Photolithographic patterning and LbL fabrication process for a patterned arrays of CNT-based electrodes.

Photolithography was first used to create a patterned (3-aminopropyl)trimethoxysilane (APTMS) film covalently bound to the Si surface. APTMS serves as the chemical anchor of the first anionic polyelectrolyte layer and was applied to the masked surface using a drop printing technique. Microcontact printing was also used to produce this anchor layer with good success. The primary amine head group on the bound APTMS was converted to a quaternary amine (R_4N^+) to create a positive charged pattern. CNTs coated with the anionic surfactant sodium dodecylsulfate (SDS) were electrostatically bonded to the pattern by solution immersion. Subsequent exposure of the pattern to polydiallyl dimethyl ammonium chloride (PDADMAC) creates a cationic layer. This process is repeated multiple times (n) to create a multilayer film of sufficient thickness to support both electronic conductivity and electrocatalytic response.

The second approach to creating CNT-based electrodes was to use filtration as a method for fabricating porous mats of carbon nanotubes. These mats represent ultrathin versions of commercial carbon papers, yet only measure several microns in thickness. One advantage to this type of structure is that a much higher density of direct physical contacts is anticipated between the CNTs resulting in higher mat electrical conductivity. Filtration deposits the CNT mat onto a mixed cellulose ester (MCE) filter membrane (Fig. 2a). The membranes can be cut into desired shapes and sizes and transferred onto a more stable support such as a glass substrate (Fig. 2b).

This relatively macroscopic level of patterning was sufficient to produce a prototype strip cell and characterize its properties, as discussed in Section 2.4 of this report.

Figure 2. Fabrication of a CNT/MCE electrode. (a) The wetted CNT-side of the MCE membrane, after filtering, has been pressed to the glass slide with Teflon filter for backing. (b) The glass slide with an attached CNT mat. The MCE has been completely dissolved and removed. Note: the CNT mats pictured were not cut to a defined geometry after filtration.

2.2 Patterned Electrode Characterization

Patterned carbon electrode arrays were fabricated on Si substrates using a layer-by-layer (LbL) assembly process. Quaternization of the APTMS pattern was used in both microcontact printing and drop printing experiments. Quaternization of the amine terminated silane placed a positive charge on the surface of the APTMS pattern, which served to promote assembly of the SDS-coated CNTs on the pattern. LbL assembled films on substrates in which the APTMS patterns did not undergo quaternization showed little to no selectivity for film assembly. The CNTs saturated the charged surface within 30 min and the substrate was removed from solution and rinsed with ultrapure water to wash away impurities and CNTs that were not strongly physisorbed.⁸ In the next step, the PDADMAC preferentially assembled on top of the SDS-functionalized CNTs. The LbL procedure was repeated until the desired number of layers was obtained.

The pattern resolution of the APTMS was the limiting factor for the resolution of the subsequent LbL CNT/polymer film assembly. Various methods were sought to create two sizes of APTMS chemical base patterns: fine patterns with minimum feature dimensions of less than one micron and coarse patterns of greater than 50 micron minimum dimension. For the fine feature patterns, microcontact printing provided the highest quality results. For microcontact printing, APTMS/EtOH solution ratios for inking of the PDMS stamp were varied from 2 % - 10 % (v/v) and it was found that 5 % created the most repeatable and highest quality chemically printed pattern. For large featured patterns, the drop coating technique proved to yield the highest quality result. It is important to note that the solution for inking the Si wafer polymer-photoresist-masked pattern during drop printing does not contain any solvents. Solvents were experimented with and only served to swell or dissolve the sacrificial polymer photolithography layer, resulting in low-quality and low-resolution patterns. After mixing the inking solution, which contains 5 % (v/v) APTMS in ultrapure water, it must be applied immediately to the Si

wafer polymer-photoresist-masked pattern. APTMS is highly reactive when exposed to water and if the 'ink' solution is left sitting more than 1 min it will no longer react with the Si to form a pattern. An attempt at creating the chemical patterns by spraying the 5 % (v/v) APTMS in ultrapure water on the sacrificial polymer photoresist was also tested. An airbrush sprayer was loaded with the inking solution and it was sprayed onto a photoresist masked Si wafer. 5-10 coats of the ink had to be applied in order for the APTMS to uniformly cover the masked Si substrate. After removal of the sacrificial polymer photoresist, the patterns were found to be extremely rough and of low resolution.

Figure 3A shows the Raman spectra of the substrate and patterned film regions of a sample where only CNT peaks are evident on the patterned area as indicated by the optical micrograph

Figure 3. Raman microspectroscopic mapping confirmed confinement of the CNT/polymer system onto the patterned substrate: (A) Raman spectra: Si (Red), CNT/PDADMAC modified Si (Black). Note that APTMS and polymer were not detected in this wavenumber range; (B) Optical micrograph of patterned LbL assembled CNT/PDADMAC film; The ability of the LbL film to preferentially order on the pattern is shown in (C) where intensity of 1590 cm⁻¹ CNT peak/Intensity of 521.5 cm⁻¹ Si peak vs. distance on patterned substrate is plotted. The $I_{\text{CNT}}/I_{\text{Si}}$ peaks in C represent the patterned LbL film displayed in the optical micrograph in B (note the matching distance axis values).

(Figure 3B). Si peaks were present in both spectra due to the micron-size sampling volume of the confocal optics. The ratio of CNT peak intensity to Si peak intensity is displayed in Figure 3C as function of distance across the patterned CNT/PDADMAC film. The peak positions shown in (Fig. 3C) correlate with the locations and positions of a CNT/polymer modified pattern on the optical micrograph (Fig. 3B).

To further investigate the ability of LbL CNT/PDADMAC films to form specifically on a pre-designated patterned area, two-dimensional Raman mapping was performed. Figure 4A displays an optical micrograph of the patterned LbL assembled CNT/PDADMAC film. Figure 4B shows a Raman false-color intensity map for the 1590 cm^{-1} peak in which CNTs are shown to favor organization on top of the charged APTMS pattern compared to the Si substrate. Figure 4C shows a high-resolution optical micrograph overlaid with a Raman map. The high-resolution image presents the selective precision for the CNTs to assemble on the quaternized APTMs. The non-uniform CNT distribution shown by the varying intensity map (Fig. 4C overlay) may be due to non-uniform APTMS concentration or quaternization of the surface pattern, or bundling of CNTs during solution deposition.

Figure 4. Optical and Raman spectral images displaying the location of the APTMS pattern and CNTs; (A) Optical micrograph of a LbL assembled CNT/PDADMAC patterned IDE film, (B) False color Raman map of (A) confirms the LbL CNT/PDADMAC film assembled selectively onto the patterned APTMS. (C) Overlay of a Raman color map on a high-resolution optical micrograph reveals the precision of CNTs to selectively assemble on the quaternized APTMS pattern. Distribution of red intensity in the Raman map can be attributed to uneven deposition/quaternization of APTMS. Scale bars are $100\text{ }\mu\text{m}$.

The intensity ratio of the CNT to Si peaks was used to determine the growth profile during subsequent LbL cycles. The linearly increasing Raman response as a function of number of

bilayers, Figure 5, demonstrates that the CNTs continue to assemble as new layers were deposited. The linear increase of CNT intensity confirms the successful addition of multiple CNT/PDADMAC bilayers, which appear to be relatively uniform for the first 8 bilayers.

Figure 5. Raman intensity shows a linear correlation between $I_{\text{CNT}}/I_{\text{Si}}$ and the number of bilayers of CNTs and PDADMAC deposited on the APTMS. An increase in the CNT Raman intensity verifies successful addition of layers to the CNT/PDADMAC film.

Atomic force microscopy was used to provide additional evidence for the presence of CNTs in the pattern. Figure 6 displays height and phase images of the patterned substrate where the morphology of the CNT dispersion is evident. These images were obtained from a pattern in which the last layer deposited was PDADMAC. An AFM image of an LbL system capped with CNTs was attempted but the tip tended to drag nanotubes across the surface resulting in significant shadowing. The nanotube bundles, seen as the bright (large height) fibers in Fig. 6a, are relatively well-dispersed in these images and provide evidence of a well-connected mat in the plane of the film. Also notable, are several isolated, prominent features in the phase image that could be exposed CNT bundle ends that may provide connections between layers as explained below.

Figure 6. Atomic force images (A – topography, B – phase) of the surface of a LbL CNT/PDADMAC patterned film. These images confirm that the surface of the patterned APTMS contains a good dispersion of CNTs. Note that the surface of this LbL pattern was last layered with PDADMAC as the CNTs are saturated with a polymer coating.

The electrical properties of the patterned composites were probed by I-V DC sweeps. Indium contacts were placed on specific locations of the pattern to ensure an ohmic contact between the pattern and probe tip as demonstrated by the linear I-V response in Figure 7.

Figure 7. 4-point probe I-V curves for multiple bilayer CNT/PDADMAC films (black = 3 bilayer, red = 5 bilayer, blue = 8 bilayer).

The resulting conductivity for a 3 bilayer film, using the resistance found from the inverse slope of the 4-point probe measurement is calculated as follows:

$$\sigma = l/(R \cdot A) = 0.2 \text{ cm}/(36359 \Omega \cdot 7.8 \times 10^{-8} \text{ cm}^2) = 70 \text{ S} \cdot \text{cm}^{-1} \quad \text{equation 1}$$

The conductivity of 70 S cm^{-1} was similar to other literature reported values for CNT/polymer wrapped composites.⁹ It is important to note that the layered film was assembled on a thermally grown SiO_2 layer, which has a surface conductivity of 10^{-10} S .¹⁰ The low conductivity of SiO_2 ensures that the substrate does not interfere with the conductivity measurement of the LbL patterns. Samples of 3, 5, and 8 bilayers were tested using 2-point and 4-point probe geometries (Table 2). For 2-point measurements, the samples' I-V characteristics were measured at three different contact spacings and the slope of the R vs. l curve was used to compute the conductivity (Figure 8 and Figure 9).

Figure 8: Thickness-normalized resistance of films with 3 (■), 5 (●), or 8 (▲) bilayers versus distance between probe points in 2-point measurements.

Figure 9: 2-point probe I-V curves (blue= 3 bilayer, black= 5 bilayer, red= 8 bilayer).

Even though this procedure is designed to minimize the influence of the interfacial resistance between the pattern and indium contact on the computed conductivity (also shown by the origin intercepts in Fig. 8), the lower 2-point values in Table 2 indicate that some interfacial resistance may still exist in the 2-point measurements when compared with the 4-point measurements. Regardless, collecting both types of data supports the accuracy of the conductivity values

reported in this work.

Table 2. 2-point and 4-point probe conductivities of 3, 5, and 8 bilayers thick films.

Bilayers	2-point s ($S\text{ cm}^{-1}$)	4-point s ($S\text{ cm}^{-1}$)
3	30	70
5	84	132
8	97	130

A significant increase in conductivity was found when the number of bilayers was increased from 3 to 5. Because the nanotubes are distributed non-uniformly within the patterned structures as shown by the Raman mapping data in Figure 4C, more nanotube to nanotube contacts are likely as subsequent layers are added. The nanotubes are primarily oriented in the plane of the structure, but some prominent features are observed in the atomic force micrographs in Figure 6, which could provide electrical contacts between layers. Therefore, as layers are added, the conductivity of the assembly increased through these interlayer CNT contacts that are woven throughout the layered structure.

2.3 Electrocatalyst Integration for an Alkaline DMFC

Using CNTs as supports for catalytic metals such as gold and platinum is well documented.¹¹⁻¹³ To create catalytically active electrodes, CNTs were functionalized with 15 wt % Au or Pt metal nanoparticles (AuNP or PtNP). Functionalization was achieved by thermal reduction of dissolved Pt or Au in the presence of the CNTs, resulting in nucleation and growth of noble metal nanoparticles on the CNT surface. Successful addition of PtNP and AuNP was characterized by transmission electron microscopy (TEM) (Figure 10).

Figure 10. TEM images of PtNP (A, scale bar 100 nm) and AuNP (B, scale bar 200 nm) supported on CNTs. The particle sizes for the PtNP and AuNPs range from 5 nm - 20 nm.

The TEM images show that the PtNP functionalized CNTs (PtCNTs) and AuNP functionalized CNTs (AuCNTs) contain metal nanoparticles ranging from 5 nm to 25 nm. Powder XRD data was used to confirm the metal species and matches that expected for nanocrystalline Pt, see Figure 11 for PtCNT sample.

Figure 11. Powder XRD pattern for a 15 wt % PtCNT sample. XRD line positions of pure Pt are shown for comparison.

Electrochemical oxygen reduction mass activity for 15 wt % PtCNT and 15 % AuCNT samples was measured at room temperature in 0.5 M KOH with the metal-CNT composite adhered to a glassy carbon rotating disc electrode (Figure 12).

Figure 12. Polarization curves for CNT-supported Pt and Au catalysts in 0.5 M KOH at room temperature (normalized for Pt or Au mass), showing a greater ORR current for the 15 wt % AuCNT sample at potentials more negative than -0.4 V vs. Ag/AgCl.

The apparent mass activity of the 15 wt % AuCNT catalyst as measured in 0.5 M KOH with air sparging was approx. 35 mA per mg Au at -0.6 V vs. Ag/AgCl compared to the apparent mass activity of the 15 wt% PtCNT catalysts which was 25 mA per mg Pt at -0.6 V vs. Ag/AgCl. This apparent mass activity for AuCNT was about 1.5 times greater than for the PtCNT sample at -0.6 V vs. Ag/AgCl. The apparent mass activities of the samples were equivalent at -0.4 V vs. Ag/AgCl.

Electrochemical methanol oxidation reaction (MOR) mass activity for 15 wt % PtCNT and 15 wt % AuCNT samples was measured at room temperature in 0.5 M KOH with 0.5 M CH₃OH with the powders adhered to a glassy carbon rotating disc electrode (Figure 13).

Figure 13. MOR curves for CNT-supported Pt and Au catalysts in 0.5 M KOH and 0.5 CH₃OH at room temperature (normalized to Pt or Au mass), showing a higher reactivity for the 15 wt % PtCNT sample.

Figure 13 shows that the PtCNT sample had significantly higher MOR activity compared to the AuCNT sample. This large difference in CH₃OH oxidation activity will allow for oxidation selectivity at a PtCNT electrode in a mixed-fuel planar fuel cell.

The resistances of the PtCNT and AuCNT samples were investigated using 4-point DC I-V measurement (Figure 14). The conductivity of a sample was calculated using equation 1 and by extracting a resistance for the slope of the resulting I-V trace. The cross-sectional areas of conduction were determined from profilometry scans and the height and width of the mat are shown in Table 3.

Figure 14. IV results from 4-point probe measurements. Unmodified CNTs (U-CNTs - red), PtCNTs (blue), AuCNTs (black).

Table 3. Sample geometry, resistance and conductivity.

	Unmodified CNTs	PtCNTs	AuCNTs
Sample length (cm)	0.75	0.75	0.75
Sample height (nm)	2000	6000	4000
Sample width (μm)	2000	1200	1200
Resistance (Ω)	34	18	31
Conductivity (S cm^{-1})	545	581	508

The samples' conductivities were all similar, $\sim 550 \text{ S cm}^{-1}$. The metal-nanoparticle functionalization is a non-covalent means of functionalization and therefore it was expected to produce minimal if any change in resistance of the samples as the metal loading was low enough not to cause percolation of the metal phase.

2.4 Electrochemical Properties of a Prototype Strip Cell

A two-dimensional fuel cell was created using CNT electrode patterning with MCE membranes (Figure 15). The AuCNTs acted as the cathode and the PtCNTs acted as the anode in the fuel

cell due their specific reactivities towards ORR or MOR as shown earlier. Cyclic voltammetry was performed on the cell with and without MeOH in basic electrolyte (Figure 16).

Figure 15. Schematic of the 2D fuel cell showing the anodic and cathodic reactions when using KOH and MeOH.

Figure 16. (A) CV response of 2D array with 0.5 M KOH (no response for a dry array). (B) CV response of 2D array with the introduction of 0.5 M KOH + 0.5 M MeOH.

The open circuit voltage (OCV) of the cell was tested as a function of time (Figure 17) and the cell was found to be sensitive to oxygen exposure.

The array's electrolyte and fuel, which are delivered to the system in a drop of liquid at 0 s, contained a finite amount of some oxygen. As oxygen in the electrolyte drop was reduced, the cell's performance declined rapidly. When oxygen was reintroduced (dashed arrows in Figure 6-8), via a pulse of air flowing over the surface of the sample, the OCV increased. It is promising that the array had a rapid response to oxygen introduction as it provides evidence that reactions are occurring at the electrodes. The stability of the cell's performance when initially provided with a large amount of oxygen was observed by introducing an air-sparged drop of electrolyte with methanol to the array (Figure 18).

Figure 17. OCV as a function of time. The arrows represent a finite introduction of oxygen to the surface of the cell.

Figure 18. OCV as a function of time. The arrow represents the introduction of a pre-oxygenated fuel source containing 0.5 M KOH + 0.5 M CH₃OH (air-sparged). The array is shown to provide a stable OCV of 0.31 V.

The introduction of pre-oxygenated electrolyte and fuel was shown to stabilize the cell's performance and decrease its dependence on the oxygen in the surrounding environment. When using an air-sparged fuel source, a stable OCV of 0.31 V was recorded for a time period for over 1 min. It is obvious that this type of cell design is oxygen limited, therefore sufficient aeration of the electrolyte is desired.

A polarization curve for the planar array fuel cell is shown in Figure 18

Figure 19. Polarization curve for the 2D planar array.

This mixed reactant fed fuel cell show low power due to the small cell size and relatively non-selective catalysts. However, the cell performance does indicate that this type of cell design has merit in terms of a creating a geometry that is advantageous for fabrication of planar 2D electrochemical arrays.

3. Two Dimensional Stack Cell

A low dimensional stack-style fuel cell is envisioned as sketched in Figure 20. The basic concept is to rely on passive transport of methanol, oxygen, and protons through opposing ultrathin, porous carbon current collectors. The focus is placed on a directional supply of fuel and oxidant over relatively short distances so that the required multi-phase boundary between solid catalyst, liquid electrolyte and O_2 gas phase is preserved at the cathode. Reactant manifolds are eliminated for this design as a CH_3OH reservoir (with H_2O) with a permeation membrane could be applied to the fuel (left) side of this cell and the oxidant (right) side of the cell is open to humid air. Water, required for the CH_3OH oxidation reaction, is supplied as a mixture with the fuel while minimal length scales at the cell cathode could be tailored to ensure evaporative loss for water generated at the cathode. The innovation addressed in this work is the implementation of the small length scales, microporous electrodes, and novel nanomaterials to enable such a passive design concept. Designs to enhance power output are anticipated from these initial studies.

Figure 20. Stack cell design for an ultrathin DMFC

3.1 Permeable Electrode Designs

Several types of permeable carbon-based electrode materials and designs were pursued to determine how they might fit within the 2-D fuel cell concept. Prototype testing of anode and cathode catalyst layers separated by 50 micron thick Nafion electrolyte film was conducted using commercial carbon papers (Toray, Japan), including graphite:Teflon coated papers. A secondary electron image of the surface of such a paper, as shown in Figure 21a, highlights the extent of microscale porosity created by the scaffold of graphite particles. Also investigated were mats made of solid carbon fibers (7 μm diameter) where inert-fiber spacing becomes the pore channels for the electrolyte and electrochemical reactants (Figure 21b). Free-standing carbon films based on pyrolyzed polymers were also investigated as potential current collectors. An example of an interdigitated array of carbon electrodes extending alternately from two electrical busses is shown in Figure 21c. A support grid framework based on electrically insulating SU8 (epoxide-based negative photoresist) has been added after carbon electrode pyrolysis to maintain a planar, film-like, free-standing structure after chemical release from the Si substrate. The microscale porosity within this type of structure comes from the open regions between the electrodes. Sufficiently thin carbon features fabricated from this process also show a degree of H₂O and CH₃OH permeability. These structures were used in strip cell configurations as an alternative to the patterned CNT electrodes described in Section 2. These patterned electrode arrays have also been used in a stacked configuration separated by 25 to 50 μm thick Nafion membranes for proton and water transport. A final variant of free standing carbon films is shown in Figure 21d where interference lithography has been used to create an inverse face centered cubic scaffold.¹⁴ Pyrolysis of the developed polymer results in a conductive carbon framework that acts as a porous electrode. The resulting scaffold can be released from the Si substrate it was created on using HF and handled as a several micron thick coherent film. Figure 21d shows an edge region of such a film folded over to highlight the free standing nature of this structure.

Figure 21. Various forms of porous carbon electrodes used in this study: a) graphite/Teflon surface of a commercial Toray paper, b) 7 mm diameter carbon fiber with a Pd electrocatalyst, c) patterned, pyrolyzed carbon electrode arrays supported by an SU8 grid framework, and d) free-standing porous carbon film formed by interferometric lithography and pyrolysis.

3.2 Electrocatalyst Integration for an Acidic Stack DMFC

The same basic requirements of enhanced, selective electrocatalytic activity apply for methanol oxidation and oxygen reduction reactions under acidic conditions as for alkaline conditions (as discussed in Section 2). Pt-Ru alloys are one of several mixed metal systems exhibiting enhanced oxidation reaction kinetics for the MOR relative to pure Pt. For this specific bimetallic system, the Ru is viewed as binding an activated surface OH species responsible for conversion of the tenaciously bound intermediate Pt-CO(H) to CO_2 – completing the full 6 electron oxidation process and freeing Pt surface sites for a subsequent cycle of CH_3OH oxidation.¹⁵ High surface area dispersions of Pt and its alloys can be created on carbon electrolytes using a wide variety of techniques. Within this limited study, methods of electrodeposition, preformed nanoparticle binding, and layer-by-layer polyelectrolyte deposition were used to integrate electrocatalysts with porous electrode structures. Examples of the types of structures possible are shown in Figure 22a-d. Where primary emphasis was placed on electrodeposition methods due to the variety of carbon films explored, LbL assembly methods to integrate pre-formed catalytic particles appear quite promising. A TEM cross section of one of these LbL assembled films comprised of 2 nm diameter Pt nanoparticles is shown in Figure 22a. The Pt particles were

functionalized with mercaptopropene sulfonate and treated as polyanion in water while polyaniline (PAni, molecular weight of 100kDa) was used as a polycation in formic acid. The bright field TEM image shows the individual particles embedded in the PAni matrix. The film has been grown to approximately 20 nm. The Pt particles are electrically wired to the carbon surface (in this case carbon fibers were used for ease of imaging) and exhibit an electroactive response for both MOR and ORR, as well as for a reversible reporter molecule like ferri/ferrocyanide. Some degree of activity scaling can be generated by controlling the number of layers used to generate the film. What makes the LbL process so appealing is the opportunity to tailor the local environment around the nanoparticles to achieve enhanced selective reactivity and to manage byproduct transport, specifically water.

Figure 22. Electrocatalyst integration onto structures within carbon electrode: a) bright field TEM image of 2 nm Pt nanoparticles attached to a carbon fiber through a LbL assembly process, b) 4 nm Pt nanoparticles covalently bound to a carbon surface using a diazonium attachment method, c) the resulting electrochemical response of the functionalized carbon surface with and without bound Pt nanoparticles, and d) PtRu nanoparticles electrodeposited onto carbon struts in a interferometric lithographically formed carbon film.

Nanoparticles can also be covalently bonded directly to a carbon surface using aromatic linking molecules. Figure 22b shows an AFM image of 4 nm Pt particles bonded to a graphite surface

through either an single aryl or diaryl linkage. A nitrophenyl diazonium salt is reacted with the graphite surface to form a nitrophenyl functionalized surface. Conversion of the nitro group to a second diazonium allows for nucleophilic attack and binding of Pt (or other metal) nanoparticles. As shown in Figure 22c, the resulting voltammetry in an acidic electrolyte yields a classic Pt response only after the nitrophenyl surface is diazotized and exposed to Pt. Electrodeposition is also a effective means of producing electrocatalytic nanoparticles. Figure 22d shows PtRu particles produced by a double potential pulse method and nucleated on the struts of an interferometric photolithographically processed, pyrolyzed carbon.

Electrocatalytic function is demonstrated for prototype stack cell design by conducting voltammetric measurements of MOR and ORR. The voltammetric data of Figure 23 highlights the benefit of using alloyed Pt-Ru particles versus pure Pt nanoparticles for methanol oxidation. In this plot, the current for CH₃OH oxidation (0.5 M in 0.1 M H₂SO₄) is displayed as a function of sweeping the potential of the electrode to more oxidizing values. The Pt-Ru particles were deposited onto a carbon electrode using a double pulse deposition method¹⁶ from a 3:1 molar mixture of PtCl₄ and RuCl₃, while 4 nm diameter Pt nanoparticles were electrostatically adsorbed to a carbon electrode. The voltammetric data shows that the Pt-Ru particles electrocatalyze CH₃OH oxidation at a lower potential when compared to the pure Pt particles. The difference in measured current reflects different electrode areas and particle loadings, as no attempt is made here to compare electrocatalytic efficiency. The observed decreased MOR overpotential (η_{MOR}) will lead to a larger cell potential at an equivalent current density when run against a common cathode in a fuel cell. The shaded area within this plot represents added available energy that is gained with this increased potential. The data additionally shows that the extent of strongly bound reaction intermediates is minimized with Ru addition to the catalyst, as evidenced by the smaller oxidative current peak observed after the potential of the electrode is reversed and scanned to more reducing potentials. This second peak is the result of oxidative stripping of the remnant reaction intermediates from the surface and is considerably smaller for the case of Ru being present. Further optimization of the Ru content leads to optimized performance with respect to methanol and yields maximum specific current densities (A·g⁻¹ of catalyst) or electrocatalytic efficiency.

Figure 23. A comparison of the reactivity to 0.5 M CH₃OH in 0.1 M H₂SO₄ for electrodeposited 3:1 Pt:Ru particles on carbon and 4 nm Pt nanoparticles that are electrostatically bound to a carbon electrode using a mercaptopropylsulfonate ligand.

Palladium was chosen as a candidate selective ORR electrocatalyst because of anticipated facile O₂ reduction and sluggish CH₃OH oxidation kinetics under acidic conditions. Methanol tolerant ORR electrocatalysts have been reviewed recently.¹⁷ Xiao et al. have recently shown that Pd grown on Au electrodes can exhibit activity that rivals Pt.¹⁸ Lamy showed that the kinetics of methanol oxidation are highly dependent on the electrolyte with acidic sulfate showing minimal activity.¹⁹ Carbon electrodes of varying type were cleaned by potential cycling in sulfuric acid until a reproducible current-potential response was achieved. These electrodes were rinsed extensively in de-ionized H₂O and transferred to a PdCl₂ solution. The carbon electrode was first stepped to an oxidative potential of 400 mV vs. Ag/AgCl to activate the surface by generating oxygen-containing functional groups at the surface.²⁰ Pd electrodeposition was conducted at -400 mV with a high rate of electrolyte convection to minimize mass transport. Figure 24a,b shows the resulting Pd nanostructures that form on carbon fibers and microporous carbon papers using this process. The Pd particles grown on both of these substrates exhibit a high surface area structure comprised of elongated needles (Figure 24a) that radiate outward. These structures are reminiscent of the anisotropic growth reported for Pd grown under hydrodynamic electrolyte flow.¹⁸ Similar structures can be grown on a variety of carbon surfaces including are also present on the Pd particles grown at the graphite particle perimeters for the gas diffusion electrode shown in Figure 24b.

Figure 24. Pd nanoparticles electrodeposited onto carbon fibers (a) and a commercial carbon paper (b). Cyclic voltammetry (c) highlights the methanol tolerance (lack of a methanol response) of this electrocatalyst in acidic sulfate. Voltammetry (d) shows the Pd particles response for ORR as being comparable to Pt.

The consequence of growing these anisotropic structures is an enhancement in oxygen reduction kinetics. Figure 24c shows a comparison of the voltammetric response of these Pd nanoparticles on carbon in the absence and presence of 0.5 M CH₃OH in an acidic electrolyte. The Pd shows the growth of a surface oxide at > 200 mV, followed by the surface oxide reduction at < 300 mV with potential scan reversal. Addition of methanol (0.5 M) produces a small increase in oxidation current that is superimposed on the current for surface oxide formation. The Pd shows high activity toward O₂ reduction in this same acidic electrolyte. Figure 24d compares the response of 4 nm Pt nanoparticles to the electrodeposited Pd nanoparticles. We note that the overpotential of ORR is larger for the Pd when compared to Pt, but facile reaction kinetics are indicated by the rate of change in current with potential. The addition of methanol to the electrolyte produces an approximate two-fold decrease in the current, indicating some degree of methanol interference. However, the relative current – potential relationship is maintained suggesting that the problem could be related to transport of O₂ to the electrode. Rotating disk voltammetry is required to separate these mass transport effects. Overall, the Pd maintains a high overall ORR activity indicating a reasonable tolerance of the presence of methanol.

3.3 Electrochemical Properties of a Prototype Stack Cell

Figure 25 shows the measured cell potential for a device based on the general stack-cell concept displayed in Figure 20. For this device, the Nafion membrane is fully hydrated with 0.1 M sulfuric acid. The Pd cathode is left open to air, and a minimal volume of 1:1 (vol) $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ is pipetted onto the back surface of the porous anode. With introduction of the methanol fuel, the cell potential decreases from a near zero value by 400 mV as methanol oxidation starts to take place. This cell potential is maintained for periods of up to 60 minutes depending on what quantity of fuel (volume) is added. Multiple traces are shown to highlight the fact that extended stable cell operation is possible, with periodic addition of fuel. The fact that the cell potential returns to a near-zero value is indicative of fuel consumption and/or extensive dilution at the anode. The voltammetry of Figure 24d clearly shows that methanol cross-over from the anode to cathode would only serve to reduce the power output of the cell by inhibiting the rate at which O_2 is reduced. We can therefore safely conclude that methanol cross-over does not contribute to the decay in cell potential. Cell potential is maintained specifically because a selective catalyst is used that is tolerant of methanol under the acidic conditions of a miniaturized PEM fuel cell. The same degree of selectivity does not exist for O_2 , as the ORR takes place on Pt-Ru alloys with only modestly reduced efficiency than on pure Pt.²¹ Some degree of cell potential decay could be a result of O_2 cross-over to the anode as the local methanol content at the anode decreases. We note that periodic replenishment of methanol at the anode extends the time duration of maximum cell potential.

Figure 25. Open circuit (cell potential under zero load) of a prototype stack cell based on 3:1 PtRu – 50 mm Nafion – Pd as a function of supply 1:1 vol. $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ to the anode.

The fact that a cell potential is developed demonstrates that these prototype devices are energy producing. An estimate of the current and power output can be gained through controlled current polarization of the electrodes. Figure 26 shows the anticipated results of cell polarization based on the performance of these electrodeposited Pt-Ru and Pd electrocatalysts on porous carbon electrodes. The cell potential is observed to decay from 400 mV for current densities (volumetric) less than $0.1 \text{ A}\cdot\text{cm}^{-3}$ to less than 50 mV approaching $0.6 \text{ A}\cdot\text{cm}^{-3}$. The corresponding power densities (volumetric) peak at $6 \text{ mW}\cdot\text{cm}^{-3}$ for a cell at approximately 200 mV and a current density of $0.25 \text{ A}\cdot\text{cm}^{-3}$. Reasonable, achievable estimates of power levels fall into the 10 mW range for device with an area of ca. 600 cm^2 (standard paper size) with $25 \text{ }\mu\text{m}$ thick electrodes separated by a $50 \text{ }\mu\text{m}$ ion transport membrane.

Figure 26. Projected voltage and power output from a stack cell prototype based on galvanostatic polarization of optimized electrodes.

4. Concluding Remarks on Alternative Electrode Structures for DMFCs

The results presented within this report demonstrate that it is possible to develop an ultrathin ($< 100 \text{ }\mu\text{m}$), essentially two-dimensional DMFC based on either a strip or stack cell design. The key elements required include porous and electrically conductive carbon-based current collectors, selective electrocatalysts for the MOR and ORR reactions, and suitable support substrates. The carbon current collectors were fabricated using novel methods of printing, filtration, spin-casting/pyrolysis to create porous electrodes. We note that our designs do not require a distinct fuel or oxidant manifold; relying on porosity of the electrodes and the cell geometry control reactant delivery. Selective catalysis, tolerant to the presence of the alternate reactant (fuel or oxidant), was achieved by growing in place, wiring pre-synthesized, and electrodepositing selectively catalytic nanoparticles into the porous electrodes. DMFCs have been demonstrated for both basic and acidic electrolytes. The devices are energy conversions devices and projected

power outputs lie in the micro- to milliwatt regimes. The power production properties of fuel cells based on these concepts will be highly dependent on scaling these devices up to and beyond areas of 600 cm^2 .

Further miniaturization is possible for these cell designs. The key is the use of optimized free-standing, porous carbon films as electrodes, such as those shown in Figure 21. We have embedded electrocatalytic nanoparticles for the interference lithographically formed carbon of Figure 21d using LbL techniques. Beyond building up the catalyst loading, the conductive polymers used to wire these particles also serve to reduce the open volume within these structures allowing for tuning of the porosity. Such catalyst assembled structures were filled with an ionomer, such as Nafion, as a semi-solid electrolyte. These LbL coated, Nafion infiltrated electrodes exhibit high activity for both MOR and ORR. Details of the interference lithography process must be addressed to make these structures more viable, including: a) the final electrode thickness is currently limited by the depth at which the lithography can be conducted and b) the antireflective layers used between the polymer and the Si substrate need to be optimized for permeability of fuel and water. A simpler approach to achieving large area, viable electrodes is the use of CNTs to form ultrathin, mechanically compliant sheets. Cui et al. have recently demonstrated solution casting techniques for creating thin film carbon electrodes onto paper and textile surfaces.²² Such a technique could be applied to Nafion impregnated materials. Equally possible is the optimization of the filtration methods discussed in Section 2 to produce large area, porous sheets comprised of CNTs, filaments and/or rope assemblies of CNTs. Cast or filtered sheets could be processed in a reel-to-reel fashion so as to incorporate electrocatalyst and laminate with ionomeric films and a polymeric fuel reservoir to produce the final stacked cell structure.

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