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14. ABSTRACT

The ultimately goal for this project is to provide the US army with a prototype of a 40W direct ethanol fuel cell (DEFC) stack using non-platinum catalysts, alkaline ionomers, and alkaline anion-exchange-membranes. Through executing this SBIR II projects, we have successfully carried out the proposed work and developed key materials for DEFC applications, which include MnO2-based cathode catalysts for oxygen reduction reaction (ORR) and Pd-based anode catalysts for ethanol oxidation reaction (EOR). Furthermore, composite membranes with an improved

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Report Title

Final Report: Development of a Direct Ethanol Fuel Cell System with Anion Exchange Membranes

ABSTRACT

The ultimately goal for this project is to provide the US army with a prototype of a 40W direct ethanol fuel cell (DEFC) stack using non-platinum catalysts, alkaline ionomers, and alkaline anion-exchange-membranes. Through executing this SBIR II projects, we have successfully carried out the proposed work and developed key materials for DEFC applications, which include MnO2-based cathode catalysts for oxygen reduction reaction (ORR) and Pd-based anode catalysts for ethanol oxidation reaction (EOR). Furthermore, composite membranes with an improved fuel crossover resistance were developed. The DEFCs using the new anode and cathode catalysts and membranes achieved peak power densities up to 150 mW cm-2 and 60% fuel energy efficiency by using optimal fuels at 90 °C. The power capacity obtained with the DEFCs that used low cost materials is comparable with state-of-the-art proton exchange membrane direct methanol fuel cells (DMFCs) that utilize expensive Pt-based catalysts and proton exchange membranes, and high-pressure oxygen gas. However, some major technical challenges still exist in developing commercializable DEFC products. A further research plan to address these challenges has been proposed in order to develop and produce 40W DEFC systems as viable products for surveillance and portable power electronics applications.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/31/2017	1	Liang Ma, Hui He, Andrew Hsu, Rongrong Chen*. PdRu/C catalysts for ethanol oxidation in anion-exchange membrane direct ethanol fuel cells, Journal of Power Sources 241 (2013) 696 - 702, ( ): 696. doi:
01/31/2017	4	Austin Strong, Courtney Thornberry,Shane Beattie, Rongrong Chen, Stuart R. Coles. Depositing Catalyst Layers in Polymer Electrolyte Membrane Fuel Cells: A Review, Journal of Fuel Cell Science and Technology, ( ): 064001-1. doi:
TOTAL:		**2**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received   Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. R. Chen* and J. Guo, “Effects of Pb on Electrocatalysis of Alcohol Oxidation Reaction on Pt/C Catalysts in Alkaline Media”, the 229th Electrochemical Society Meeting, San Diego, California, May 29 – June 2, 2016.
2. R. Chen* and J. Guo, “Effects of Pb in Electrocatalysis of Ethanol Oxidation Reaction on Pd/C and PdRu/C Catalysts in Alkaline Media”, the 229th Electrochemical Society Meeting, San Diego, California, May 29 – June 2, 2016.
3. R. Chen* and J. Guo, “Hybrid Anion-Exchange-Membranes for Direct Ethanol Fuel Cells”, the 226th Electrochemical Society Meeting, Cancun, Mexico, Oct. 5-9, 2014.
4. L. Ma, A. Hsu and R. Chen, “Performance of PdRu/C Anode Catalyst for Anion-Exchange Membrane Direct Ethanol Fuel Cells”, the 224th ECS meeting, San Francisco, Oct. 29 – Nov. 1st, 2013.
5. R. Chen, “Carbon-Supported AgCo Catalysts for Oxygen Reduction Reaction in Anion Exchange Membrane Fuel Cells”, the 224th ECS meeting, San Francisco, Oct. 29 – Nov. 1st, 2013.

Number of Presentations: 5.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received		Book Chapter
01/31/2017	5.00	Rongrong Chen, Junsong Guo, Andrew Hsu. Chapter 15. Non-Pt Cathode Electrocatalysts for Anion-Exchange-Membrane Fuel Cells, London: Springer-Verlag London, (2013)

TOTAL: **1**

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

The research results obtained through this project allow us to move the technology to the next step: designing and building prototypes for the targeted applications. The technology transfer includes the following strategies:

1. Target surveillance and portable power applications: Alkaline anion exchange membrane fuel cells (AAEMFCs) have the potential to replace proton exchange membrane fuel cell (PEMFC) technology or lithium batteries as the new power source of the future. The direct ethanol fuel cell (DEFC) technology based on alkaline anion exchange membranes (AAEMs) and low-cost non-platinum catalysts, developed by Tremont Technology, holds great potential in both military and commercial markets. The first product of AAEM-DEFCs will be for surveillance and portable power applications (5-50 W). The performance and durability of this product is expected to be similar or better than the PEM-based DEFC products with a fraction of the cost. The current readiness level (using DOD terminology) for this product development is 6.3. Scale down (1-3 cells) prototypes were built and tested under various operational conditions in the laboratory. The peak power density of 150 mW cm-2 and energy capacity of 100 mWhr per cm2 of MEA with one gram of ethanol fuel have been achieved with our AAEM-DEFC single cells assembled with the developed MnO2-based cathode catalysts and Pd-based anode catalyst. Key technical hurdles were identified that includes the flooding of cathode, the efficiency of ethanol oxidation reaction, and manufacturing cost of the fuel cell stacks and systems. After successfully addressing these challenges, we aim to develop commercial viable portable power applications to replace PEM-direct ethanol fuel cell or direct methanol fuel cell products within two years.

2. Industry analysis: For the most part, the fuel cell industry has been surviving on government grants and support from many nations for two reasons: (1) the entry point is high due to the long development stage, and (2) the cost of the PEMFC products has been prohibitively expensive. Since Tremont Technology has extensive experience with the proposed product, we do not foresee the first point as an issue, and the proposed product effectively addresses the second point. Reducing manufacturing costs and designing products with packaging flexibilities that meet requirements from different customers are the key project tasks. Developing new manufacturing techniques, such as 3D printing, will allow us to produce prototypes efficiently and economically.

3. Potential market: The size of the market for affordable fuel cells is unknown, as it is uncharted and untested. But the application of our product to portable electronics, when mature, can easily be on par with lithium ion rechargeable batteries, which today has a world market of about $50 billion. The advantages of fuel cells over lithium ion batteries include no down time to recharge, long run time with sufficient fuel supplies and no heat signatures. Current the lithium ion battery packs for electric vehicles are about 450-$550/kWh, but our targets reduce this to $100/kWh. When the DEFC products can be demonstrated to achieve the energy capacity and maintain costs similar to the lithium ion batteries, they will be ready to be introduced into some of the lithium ion battery markets, which includes portable electronics, distributed power generation suitable for farm and commercial building applications, and vehicle applications. Additionally, the developed membrane and catalyst technologies will transition into great potentials for metal-air battery applications, a global market projected to reach $1.7 billion in 2018.

4. Investments: For the prototype products, roughly $500,000 per year, for two years will be required for: (1) hiring technicians and engineers, (2) purchasing materials, tools and essential equipment for assembling and testing AAEM-DEFCs, and (3) working with partners, such as Faraday Technology, Protonex and Ultracell. After the 40W AEM-DEFC prototype is successfully demonstrated in the lab, more units of the prototypes will be produced and placed in field test. A bill of materials will be developed and applied to estimate system efficiency and costs. Production processes for making catalysts, membranes, MEAs, DEFCs, and DEFC stacks will be designed, installed and tested.

5. Path to commercialization: In two years, a mature prototype of a 40 W AAEMFC system, high-performance yet low-cost catalysts, and polymeric electrolytes for oxygen (air) electrodes will be ready for demonstration, small-scale production, and market testing. Investment in scaling up production and marketing will be identified. Longtime partners such as Faraday Technology Inc. (Clayton, Ohio), Protonex and Ultracell have agreed to support technology transfer from the cell to stack and systems. With their extensive manufacturing and commercialization experiences, we are confident that the developed technologies will be become viable products.

Final Technical Report
W911NF-13-C-0062 **Tremont Technology, Inc.** **Proposal A2-5140**

Development of a Direct Ethanol Fuel Cell System with Anion Exchange Membranes

By Rongrong Chen (PI)

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Final Report

INTRODUCTION

The United States Military Forces have great needs for electrical power during extended operations. Currently, the power is provided by either internal combustion powered generators or secondary batteries. Fuel cell technology as a clean and efficient energy source has several advantages for military applications, including lower weight, better safety, shorter down time (no recharge time, unlike secondary batteries), and lower heat signature (as compared to combustion engines). Direct methanol fuel cells (DMFCs) based on proton-exchange-membranes (PEMs) have been widely studied and proven successful to a certain extent. The key barriers to DMFCs for military applications include low energy/power density and high cost due to the usage of platinum-based catalysts and expensive membranes. Ethanol not only has a 33% higher energy density than methanol, but also has the advantage of being nontoxic and less flammable, which are attractive features for both military and commercial applications. Additionally, ethanol can be produced by fermentation of locally-sourced biomass, such as food wastes or agricultural wastes, which will reduce military vulnerability due to needs to transport fuels in combat fields.

Recent research demonstrated that direct ethanol fuel cells (DEFCs) based on alkaline anion exchange membranes (AAEMs) can achieve higher power capacities than PEM-DEFCs. Compared to the harsher acidic environment of PEM fuel cells, AAEM fuel cells have an intrinsic advantage in oxygen reduction reaction kinetics in which less expensive non-Pt electrocatalysts such as Pd, Ni, Co, Ag, macrocycles, or MnO_2 can be used. Also, the ethanol oxidation rates are faster in an alkaline media than in an acid media. By employing non-noble metal cathode catalysts with excellent ethanol tolerance, high concentration ethanol solution can be used as the anode fuel without the usual negative effects from ethanol crossover, which is an essential new feature that allows the AAEM-DEFC stacks to achieve much higher energy densities.

The objectives of this Phase II project included (1) to screen and demonstrate performance and durability of essential materials, including cathode and anode catalysts, anion-exchange-membranes and ionomers for meeting application requirements in DEFCs; (2) to study and prove the design concepts of components for single DEFCs and DEFC stacks; (3) to investigate fuel cell operation conditions (fuel compositions, temperatures and gas pressures) for the performance of DEFCs. Five research tasks proposed in Phase II research plans were carried out, including: (1) the preparation and optimization of catalysts for oxygen reduction reaction (ORR) and ethanol oxidation reaction (EOR); (2) the development of thermal/electrochemical stable membranes and ionomers; (3) minimizing the need of KOH in ethanol fuels; (4) scale-up of pilot production of catalysts and membranes for prototype DEFC stacks and (5) designing, fabricating and testing DEFC stacks.

The most important results from this Phase II project are summarized as follows.

1. Developed Low-Cost yet High-Performance Cathode and Anode Catalysts

1.1A. Catalysts for Oxygen Reduction Reaction (ORR)

After screening several catalyst systems [ref. to publications 1-3], including Pd-based, Ag-based, macrocycles and MnO_2-based, We discovered and demonstrated that MnO_2-based cathode catalysts had the best ORR activity than other cathode catalysts in strong alkaline-AAEM-DEFCs, which is a key advantage for manufacturing commercial DEFC products since MnO_2 is a low cost material (less than $900/ton). In a strong alkaline media, Pt–based cathode catalysts were found to have high ORR activation over potentials due to strong OH- adsorption under AAEM-DEFC test conditions. Also Pt-based cathode catalysts could be poisoned easily by the cross-over ethanol fuels. In contrasts, MnO_2 had excellent OH- and ethanol tolerances and thus superior ORR activity/stability in AAEM-DEFCs. The most recently, we discovered that MnO_2 treated with transition-metal macrocyclic (MPc) molecules had significantly longer run time and higher energy capacity than the MnO_2 cathode catalyst without MPc treatments in DEFCs.

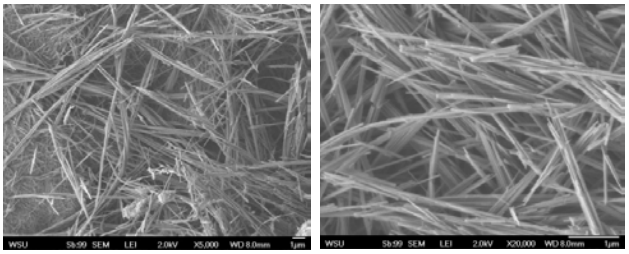


Fig. 1. Scanning electronic microscopy (SEM) images of the synthesized MnO_2 with designed composition and morphology.

A large quantity of MnO_2 with preferred morphology and composition were prepared and tested in DEFCs. Fig.1 shows scanning electronic microscopy (SEM) images of the MnO_2 with the preferred α-form and morphology. Fig. 2 shows the ORR polarization curves obtained with a rotating ring disk electrode (RRDE) coating with various catalysts. The α-MnO_2 (labeled as M-180C-12H-K in Fig. 2) shows the best ORR activity, almost as good as Pt/C (50% wt.). Under constant current discharge (300mA cm^{-2}) at room temperature, the electrodes with Pt/C catalysts show a steady voltage around 0.200 V vs. Hg/HgO and the electrodes with MnO_2/C catalysts show a voltage around 0.23-0.25 V vs. Hg/ HgO without significant voltage drops for 300 hours (Fig. 3a and 3b). Stability tests of electrodes with Pt/C vs. MnO_2/C cathode catalysts at 70°C show significant voltage drops for both catalysts (Fig. 3c and 3d). The voltage drop with the Pt/C electrode (Fig. 3c) seems to be more rapid than that with the MnO_2/C electrode. The electrodes were also tested for ethanol

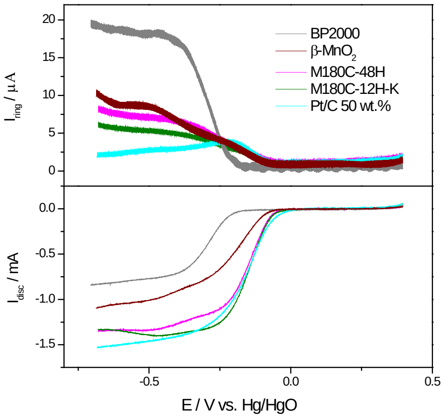


Fig.2. ORR polarization curves of MnO_2 catalysts with different composition and morphology on a RRDE with a rotation rate of 2500 rpm in O_2 saturated 0.1 M NaOH. Ring potential E_r = 0.3V vs. Hg/HgO; Scan rate 10 mV s^{-1}.

poisoning at 0.5M ethanol concentrations with constant current 50 mA cm^{-2}. The performance (Fig. 4) showed a reasonable degree of stability throughout the test for both Pd/C and MnO_2/C electrodes, but rapid voltage drops were observed on the Pt/C electrode. The RRDE and half-cell measurement results indicate that the optimized MnO_2/C catalyst has promising ORR activity and stability to replace bench-mark Pt/C catalysts for DEFC applications. By using the accelerated stability test protocol, the run time of DEFCs using MnO_2/C vs. transition-metal macrocyclic molecule modified MnO_2/C cathode catalyst at 90°C with 100 mA cm^{-2} discharge current density is shown in Fig.5. The cell voltage drops were found to be due to the anode fuel crossover that could flood the cathode and block the gaseous channel of O_2, resulting in increasing ORR overpotentials. Macrocyclic molecules modified cathodes improved hydrophobicity of the cathode catalyst layer and so better fuel crossover tolerance and longer run time in the DEFC.

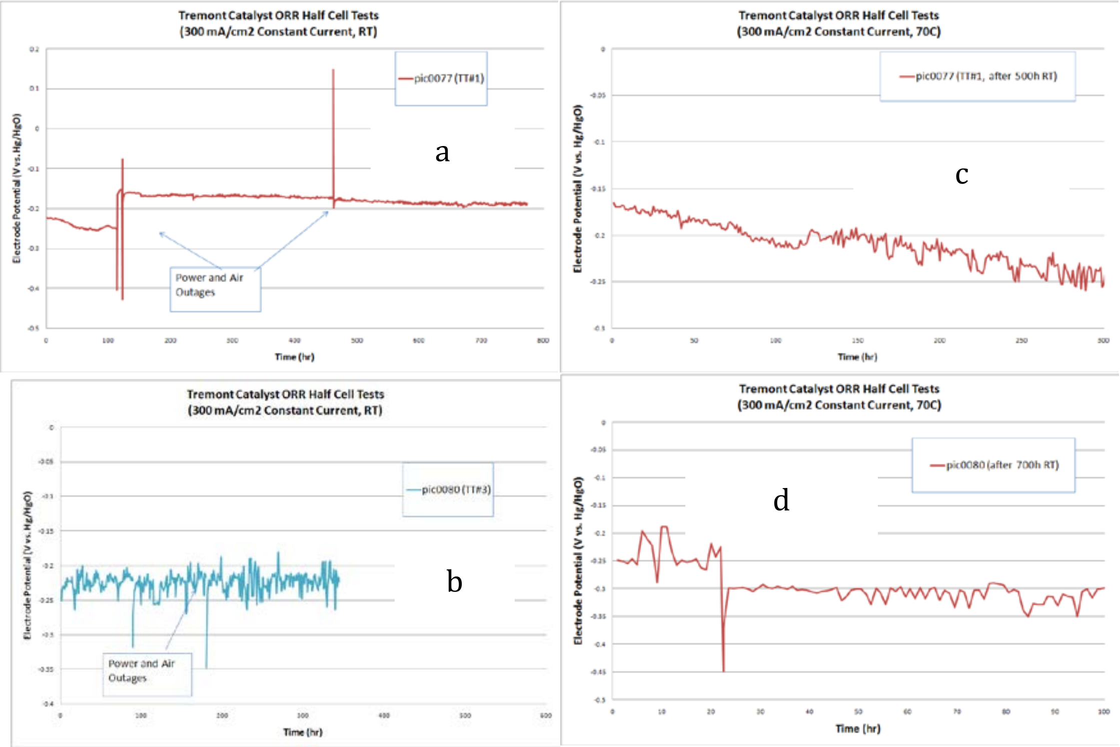


Fig.3. Long-term stability test on various catalysts with 300 mAcm^{-2} current density at room temperature and 70°C, respectively. (a) and (c) 40% Pt/C catalyst; (b) and (d) MnO_2/C.

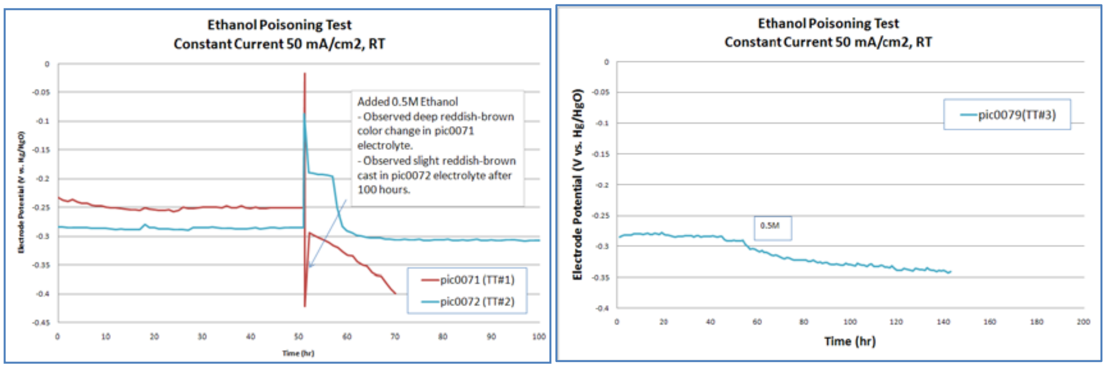


Fig.4. Ethanol poisoning test at constant current 50 mA cm^{-2} at room temperature. TT#1 = Pt/C electrode; TT#2 = Pd/C electrode; TT#3 = MnO_2/C electrode.

1.1B. Catalysts for Ethanol Oxidation Reaction (EOR)

Besides identifying the most promising cathode catalysts, we also developed and tested a large number of promising anode catalysts for EOR in alkaline media and discovered some fundamental differences in electrocatalysis of EOR on various catalyst systems, including Pt/C, Pd/C and Rh/C. The effects of additives, such as Pb and Cu, in various catalyst systems were also investigated in details. The Pd-based catalysts were demonstrated to be the most active and stable anode catalysts for the EOR in alkaline media. Both Pt and Rh-based catalysts tend to be easily poisoned by the EOR intermediate products, such as acetaldehyde or CO, while Pd-based catalysts are capable of oxidizing acetaldehyde efficiently. Some of these research results have published and others have been prepared for the publication soon [ref. 4-6].

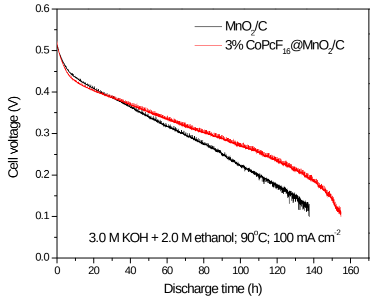


Fig.5. Accelerated stability test of DEFCs assembled with Tokuyama's A201, 20% Pd/C anode catalysts, 50% MnO_2/C vs. $CoPcF_{16}$ modified 50% MnO_2/C cathode catalyst by circulating 500 ml of 2M ethanol and 1M KOH fuel and discharging at 100mA cm^{-2} at 90°C.

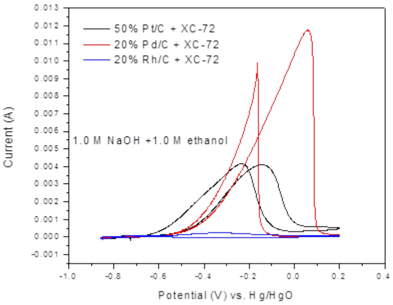


Fig.6. Cyclic voltammogram (CV) curves obtained on anode catalysts (Pt/C, 20% Pd/C and 20% Rh/C) in 1M NaOH and 1M ethanol solutions at room temperature. Scanning rate: 20 mV sec^{-1}.

As shown in Fig.6, the Pd/C catalysts were found to have the highest peak current in cyclic voltammograms (CVs) as in comparisons with Pt/C and Rh/C catalysts. The current and voltage polarization and power curves obtained with the DEFCs using the same MnO_2/C cathodes and membranes, but various anode catalysts are shown in Fig. 7. Unexpectedly, the DEFC using the Rh/C anode catalyst showed the highest peak power density (>200 mW cm^{-2}), while that with the Pt/C anode catalyst had the poorest performance. The stability tests of DEFCs with the Rh/C and the Pd/C anode catalysts indicated that the DEFCs with the Pd/C anode catalyst degraded at a much slower rate than those with the Rh/C anode catalyst. As shown in Fig.8, the cell voltage of the

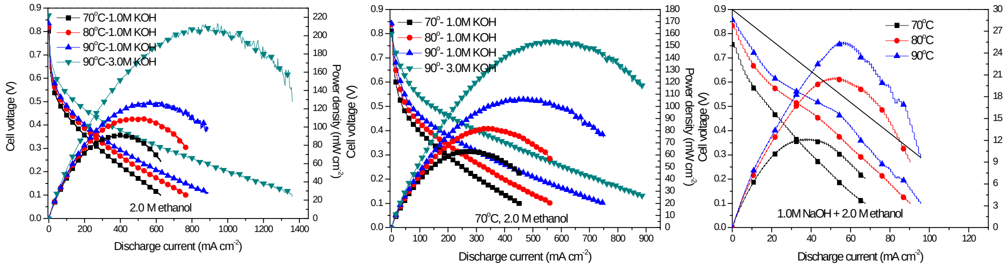


Fig.7. Polarization and power density plots of AAEM-DEFCs using 2.0 M ethanol doped with 1 M or 3M KOH. Anode: 0.5 mg cm^{-2} metal loading, cathode: 1.3 mg cm^{-2} MnO_2/C (50 wt.%), Tokuyama's A201 membranes, Tokuyama's A4 ionomer. Cathode gas: humidified O_2 (300 ml min^{-1}), Temperature: 70, 80 and 90°C.

DEFC with the Rh/C anode catalyst dropped rapidly to 0.1 V, while the DEFC with the Pd/C anode catalyst could run up to 70 hours. By preparing mixtures of Rh/C and Pd/C at weight ratio of 15 to 5, 10 to 10 and 5 to 15, respectively, the stability test results revealed that the anode catalyst with the higher Pd contents led to slower degradations in the accelerated stability test. Although Rh/C anode catalysts had higher initiate performance, they were not stable and lost their EOR activity rapidly under the accelerated stability test conditions. Since the fuel solutions were circulated, they could be collected for EOR product analysis. As shown in Fig.9, the colors of the collected fuel solutions from the DEFC using the Rh/C anode catalyst were very different from that with the Pd/C catalyst. These results led us to perform further fundamental investigations of electrocatalysis of EOR on various catalyst systems.

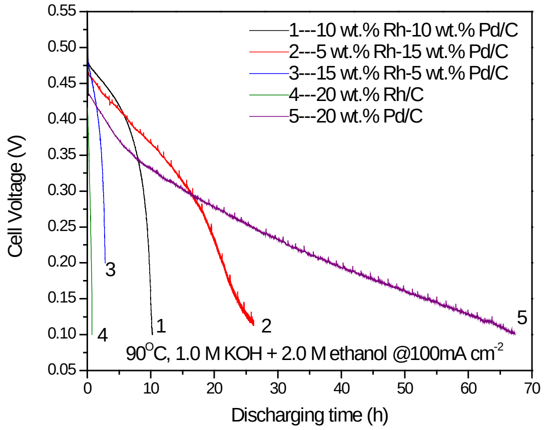


Fig.8. Cell voltages as the function of discharge time by circulating 500 ml of a 2M ethanol and 1M KOH fuel and discharging at 100mA cm^{-2} at 90°C. MEAs prepared with various anodes, same MnO_2/C cathode and A201 membranes.

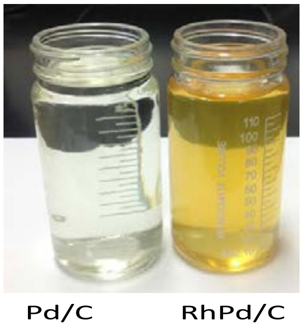


Fig.9. Fuel solutions collected after the stability tests.

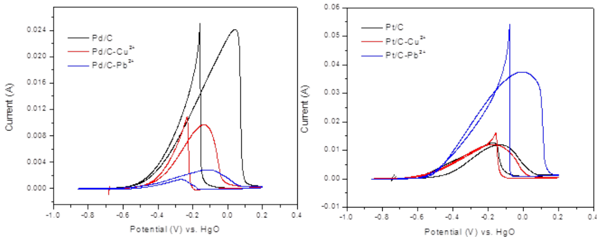


Fig.10. CV curves obtained with (a) Pd/C catalyst and (b) Pt/C catalyst in an Ar-saturated 1.0 M EtOH and 1M NaOH solution, or an Ar-saturated 1.0 M EtOH and 1.0M NaOH and 1.0 mM $CuSO_4$ solution or an Ar-saturated 1.0 M EtOH and 1.0M NaOH and 1.0 mM $Pb(CH_3COO)_2$ solution. Scan rate: 20 mV sec^{-1}.

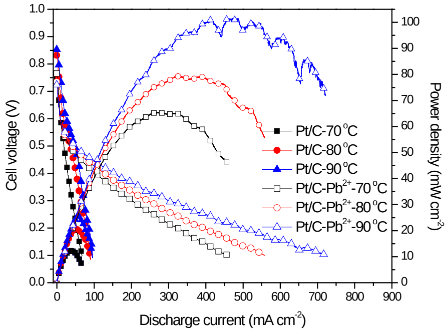


Fig.11. Polarization and power density plots of AAEM-DEFCs using 2.0 M ethanol doped with 1 M KOH without and with Pb^{2+} additions. Anode: 0.5 mg cm^{-2} Pt loading, cathode: 1.3 mg cm^{-2} MnO_2/C (50 wt.%), Tokuyama's A201 membranes, Tokuyama's A4 ionomer. Cathode gas: humidified O_2 (300 ml min^{-1}), Temperature: 70, 80 and 90°C.

As shown in Fig. 10, additions of Pb^{+2} in the ethanol fuel solutions were found to increase the EOR currents very significantly for the Pt/C catalyst, but had opposite effects on the Pd/C catalysts. The addition of Cu^{2+} in the ethanol fuel solution did not have significant impacts on the EORs on the Pt/C catalyst but hindered the EOR on the Pd/C catalyst. The I-V polarization curves and power density curves obtained with the Pt/C anode catalyst in the 2M ethanol and 1M KOH fuels without and with Pb^{2+} additions are shown in Fig. 11. Agreed with the CV results, the DEFC using the fuel containing Pb^{2+} showed 5 times higher peak power density than that using the fuel without Pb^{2+} additions. The accelerated stability tests were shown in Fig.12, which revealed that the Pb^{2+} addition in the fuel slowed the degradation of the Pt/C anode catalyst, but still ran much less time that the Pd/C anode catalyst that could run up to 70 hours under the same test conditions (Fig.8). The collected fuel solution after three hours of stability test with the Pt/C anode catalyst using Pb^{2+} containing fuels was dark yellow, which was mainly due to the polymerization of acetaldehyde in a strong alkaline media. Also shown in Fig.12, the cell voltages dropped at a much slower rate for Pd/C anode catalyst using a Pb^{2+} containing fuel but had ~50 mV lower initial voltages in the first 10 hours. Although Pd_2Ru anode catalysts showed slightly higher initial performance, their cell voltages dropped much faster than those with the Pd/C catalysts in the accelerated stability tests. It has become an evidence that neither the CV tests nor the DEFC initial performance tests are adequate to screen and select anode catalysts. **Instead, it is essential to run the accelerated stability tests to determine the optimal materials for DEFC applications.**

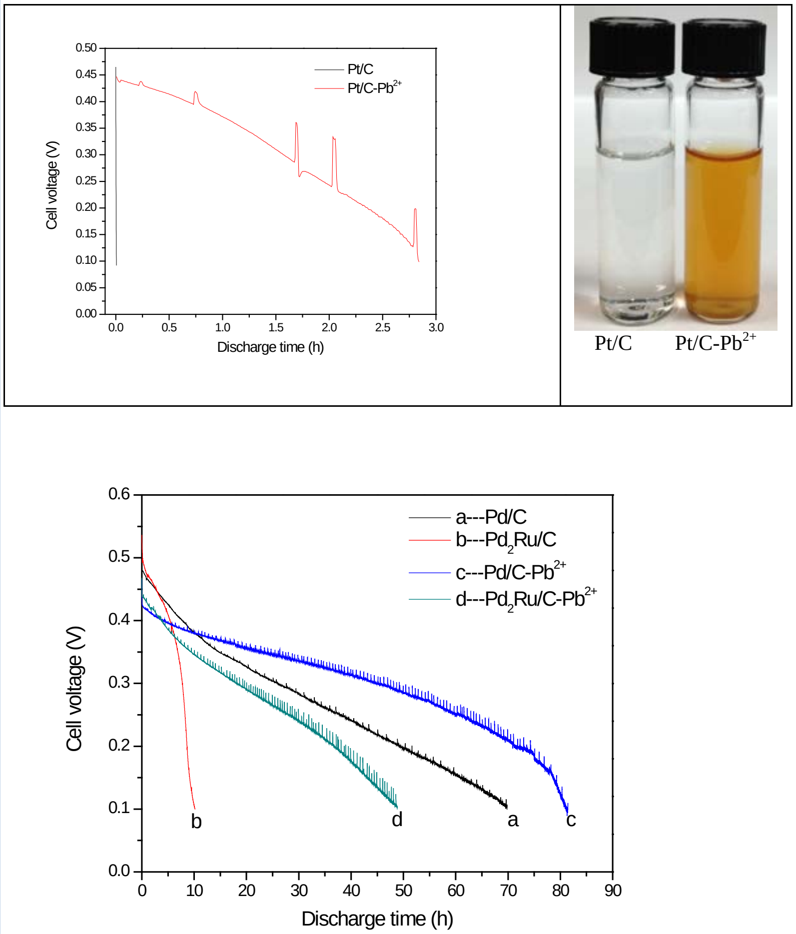


Fig.12. Cell voltages as the function of discharge time by circulating 500 ml of a 2M ethanol and 1M KOH fuel without and with Pb^{2+} additions and discharging at 100mA cm^{-2} at 90°C. MEAs prepared with Pt/C or Pd/C or Pd2Ru/C anode, MnO_2/C cathode and A201 membranes.

Since Pb^{2+} is a hazard material for our environment, we further studied other additives to improve the EOR on the Pd-based catalyst. As shown in Fig.13, the run time of a DEFC with a Cu modified Pd/C anode catalyst was increased up to 95 hours. Through details of fundamental studies of the electrocatalysis of EOR on various catalysts, it was found that the ability to oxidize EOR intermediate products, such as acetaldehyde or CO, is the key to determine the stability of the anode catalysts in DEFCs. As shown in Fig. 14, the starting oxidation potential of acetaldehyde on the Pt/C catalyst is about 200 mV more positive than that on the Pd/C catalyst. With the Pb^{2+} addition in the electrolyte, the oxidation potential of acetaldehyde is shifted to 200-250 mV lower potentials. Additing either Pb^{2+} or Cu^{2+} in the electrolyte also shifts the oxidation potential of acetaldehyde on the Pd/C catalyst, which could explain the improved stability of the Cu-modified or Pb-modifed Pd/C anode catalysts in the DEFCs.

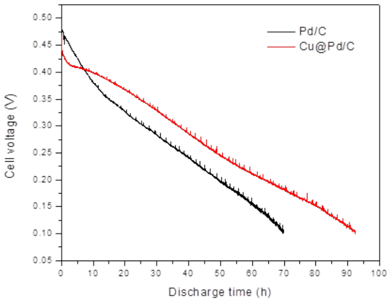


Fig.13. Stability test by recording cell voltages during discharging direct ethanol fuel cells with Pd/C or Cu-modified Pd/C anode catalysts and circulating 500 mL fuels at constant discharge current density of 100 mA cm^{-2} and 90 ^{o}C. The fuel contains 2M EtOH and 1M KOH.

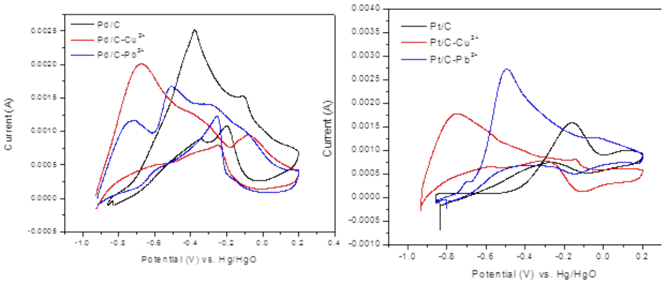


Fig.14. CV curves obtained with (a) Pd/C catalyst and (b) Pt/C catalyst in an Ar-saturated 1.0 M CH_3CHO and 1M NaOH solution, or an Ar-saturated 1.0 M CH_3CHO and 1.0M NaOH and 1.0 mM $CuSO_4$ solution or an Ar-saturated 1.0 M CH_3CHO and 1.0M NaOH and 1.0 mM $Pb(CH_3COO)_2$ solution. Scan rate: 20 mV sec^{-1}

Based on the accelerated stability test results, we consider Pd/C catalysts as the optimal anode catalysts for building the prototype DEFC stacks. For pilot production of large quantities of the Pd/C catalysts, it is important to understand the stability of the catalyst material during storage. As shown in Fig.15, the x-ray differaction (XRD) spectra were obtained on the sample freshly made and stored up to 83 days. Compared with the freshly prepared Pd/C sample, the oxide peak was quite significant on the aged sample. Fig.16a shows the cyclic voltammetry curves obtained with the fresh and aged Pd/C catalysts, respectively. Significantly larger oxide reduction peak and hydrogen desorption peak were observed on the aged Pd/C catalyst, which agree well with the XRD results that surface oxide was formed on the Pd surface. Surprisingly the fuel cell performance (Fig.16b) using the aged Pd/C anode catalyst was found to be significantly better than the fresh one. Further investigations will be needed to understand the effect of surface oxide

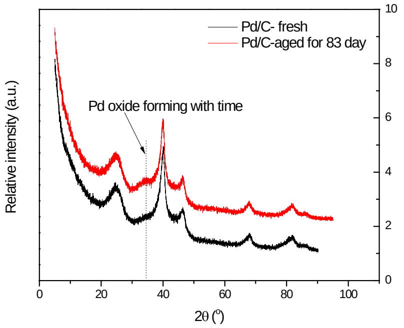


Fig.15. X-ray diffraction spectra obtained with the Pd/C catalyst stored for an extended period.

on the Pd/C toward EOR electrocatalysis. Developing reliable methods to characterize the composition and morphology of the prepared Pd/C anode catalyst will be one of the main tasks in the future research.

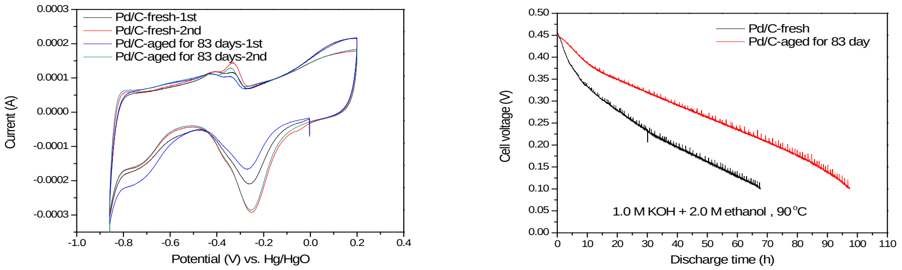


Fig. 16. (a) CV curves obtained with fresh and aged Pd/C catalysts in an Ar-saturated 1.0 M CH_3CHO and 1M NaOH solution. Scan rate: 20 mV sec^{-1} (b) Stability test by recording cell voltages during discharging direct ethanol fuel cells with fresh or aged Pd/C anode catalysts and circulating 500 mL fuels at constant discharge current density of 100 mA cm^{-2} and 90 ^{o}C. The fuel contains 2M EtOH and 1M KOH.

2. Developed Composite Membranes with Improved Fuel Cross-Over Capacity For DEFCs

The SEBS-based membranes and ionomers were demonstrated to have comparable performance to the current commercially available Tokuyama's membranes and ionomers in DEFCs, and can be operated at temperatures up to 90°C. Scale-up for preparing these membranes and ionomers were carried out during Phase II. The swelling of AAEMs during operating DEFCs was found to be a key factor causing the degradations of the cell voltages. The resistance of crossover of anode fuels in an AAEM was found to have great impacts on the run time and energy capacity of the DEFCs. Although MnO_2-based cathode catalysts do not have EOR electrocatalytic activity, the fuel crossover tends to flood the cathode and blocks gaseous O_2 reaching onto the catalyst active sites, which could cause rapid cell voltage drops. New strategies with improved stability of AAEMs and longer run time in DEFCs were tested and validated.

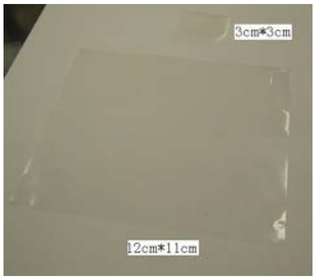


Fig.17. Variously sized anion-exchange-membranes casted by using a "home-made" device.

As shown in Fig. 17, SEBS-based AAEMs of various sizes were casted with a customized device built in our lab. Compared to the polysulfone membranes, the SEBS-AAEMs have better mechanical strength, less swelling and much better performance in DEFCs. As shown in Fig. 18, SEBS-based membranes with various thicknesses have been successfully prepared and tested in the H_2/O_2 fuel cells that used the same cathodes and anodes. The titration results indicated the ion exchange capacity (IEC) to be 0.78 mmol g^{-1}. Unexpectedly, the thicker membranes showed better fuel cell performance. As shown in Fig. 19, SEBS-based ionomers with various IECs were tested in H_2/O_2 AAEM fuel cells using the A901 membranes and the same anodes and cathodes. As shown in Fig.18a, the AAEMFCs assembled with the anode and cathode using the ionomers with the IEC at 1.3 mmol g^{-1} had the least voltage losses and the highest power densities. The AAEMFC with the anode prepared with the high IEC ionomer and the cathode with the low IEC ionomer had the worst voltage losses and the lowest power density.

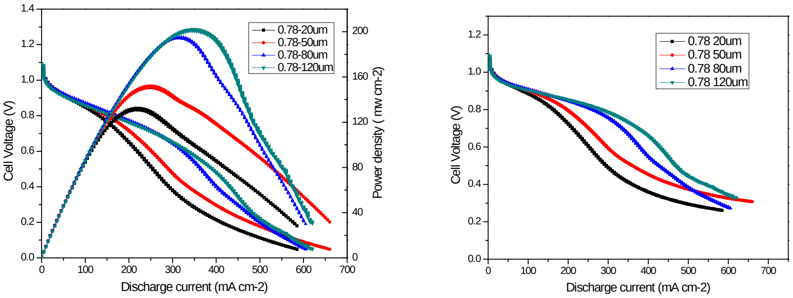
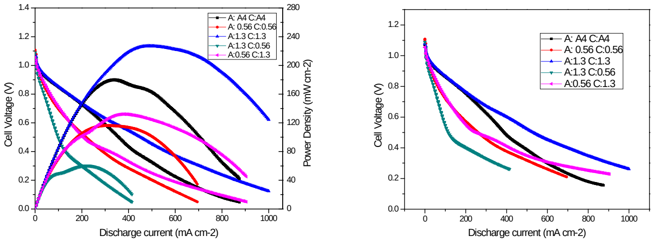


Fig.18. (a) I-V polarization curves and power curves of MEAs fabricated with QSEBS membrane (IEC: 0.78). Test conditions: Pt loading 1 mg cm^{-2} for both the cathode and anode; cell and H_2/O_2 humidifier temperatures 50 ^{o}C; H_2 and O_2 flow rates 0.2 L min^{-1} at 20 psi backpressure and 100% RH. (b) IR-corrected I-V curves shown in (a).



(a) (b)

Fig.19. (a) I-V polarization curves and power curves of MEAs fabricated with QSEBS ionomers that had various IECs. Test conditions: Pt loading 1 mg cm^{-2} for both the cathode and anode; cell and H_2/O_2 humidifier temperatures 50 ^{o}C; H_2 and O_2 flow rates 0.2 L min^{-1} at 20 psi backpressure and 100% RH. (b) IR-corrected I-V curves shown in (a).

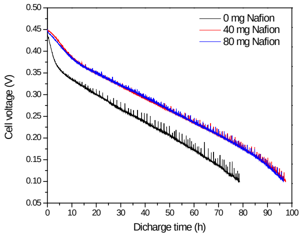


Fig.20. Cell voltages as the function of discharge time by circulating 500 ml of a 2M ethanol and 1M KOH fuel and discharging at 100mA cm^{-2} at 90°C. MEAs prepared with a 20% Pd/C anode, MnO_2/C cathode, A201 membrane treated with various amounts of Nafion solutions.

Because ethanol oxidation reaction consumes OH- ions, it becomes inevitable to add KOH or other forms of OH- ions in the ethanol fuel in order to achieve targeted power and energy capacity of DEFCs. Due to the presence of KOH in the ethanol fuel, the design criteria of alkaline anion exchange membranes (AAECs) for the DEFCs were found to be different from what was optimized for H_2-O_2 fuel cells. For example, the resistance of crossover of anode fuels in an AAEM has great impacts on the run time and energy capacity of DEFCs. As shown in Fig.20, our recent attempts to reduce the fuel crossover by treating the AAEMs with Nafion sprays were found to be effective to achieve 50 mV higher cell voltages and 20 hours longer run time than the membranes without the Nafion modifications. Further investigations are in progress to further improve the performance and stability of the AAEMs for the DEFC applications.

3. Developed an Accelerated Stability Test Protocol

An accelerated stability test of key materials was developed by discharging the DEFC at current density of 100 mA cm^{-2} and 90 °C by using a 500 mL circulated ethanol fuel. As shown in the prior sections, this accelerated test was demonstrated not just to be very useful to evaluate the tolerance of impurities of anode catalysts since the fuel is circulated, but also can be applied to determine the stability of membranes and overall fuel efficiency. Through the collection of circulated fuel solutions, we discovered the fundamental differences of EORs on the Pd-based catalysts verses the Pt-based catalysts. The test protocol can be routinely used to evaluate the key materials and components for DEFC applications.

4. Optimal Fuel Compositions and Fuel Cell Operational Conditions for High Power/Energy Capacity of DEFCs

Toward the end of phase II project, we have identified the most promising cathode and anode catalysts that not just show high initial energy and power capacities but also have the lowest degradation rate in the accelerated stability test. Because ethanol oxidation reaction consumes OH^- ions, the addition of KOH or other forms of OH^- ions in the ethanol fuel has become essential in order to achieve desired power and energy capacity in DEFCs. The effects of fuel compositions on the initial performance and stability of the DEFCs were studied comprehensively and shown in Fig. 21. Increasing KOH concentrations from 1M to 3M in the ethanol fuels resulted in about100 mV higher cell voltages and significantly higher peak power densities. The accelerated stability test also showed the significant longer run time and higher cell voltages by using the ethanol fuel containing 3M or higher KOH. For the simplicity and cost of the DEFC operating system, low KOH concentration in the fuel is desirable. Without circulating the fuel in a practical system, the run time of DEFCs will be further increased since the reaction products or impurities will not be accumulated with the rate as those with the circulated fuels in the accelerated stability test. When fresh ethanol fuels with the desired concentrations are used, the DEFCs should achieve optimal and stable cell voltages till the fuels are completely consumed.

As discussed in the previous section, reducing fuel crossover from the anode to the cathode with the hybrid membranes could increase the cell voltages up to 50 mV with 100 mA cm^{-2} discharge current, which is equivalent 5 mW cm^{-2} higher power density. Fuel crossover could also happen if the MEAs were not sealed well. Improved sealants were found to reduce the cell voltage losses significantly and will be further investigated.

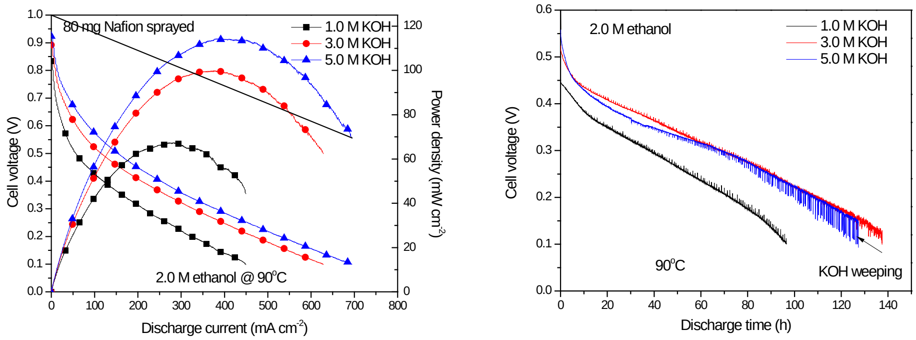


Fig.21. (a) I-V polarization curves and power curves of MEAs prepared with a 20% Pd/C, MnO_2/C cathode, treated A201 membrane and 2M ethanol and xM (x = 1, 3, 5) KOH fuel at 90°C, respectively. (b) Accelerated stability test of the DEFCs by circulating 500 ml of 2M ethanol with xM (x=1, 3, 5) KOH discharged at 100mA cm^{-2} at 90°C.

5. Explored New Manufacturing Techniques to Fabricate Parts for DEFCs

The manufacturing techniques for making membrane electrode assemblies (MEAs) were studied and published in Ref.7. New methods to fabricate parts for fuel cells were explored. With the development of new desktop 3D printers, the use low-cost 3D printing is now viable for design and production of many products. Recently Chisholm and others reported the production and operation of a PEM electrolyser constructed from silver coated 3D printed components fabricated from polypropylene [4]. They believe that the approach allows construction of light weight, low cost electrolysers and the rapid prototyping of flow field design. They also presented data on the operation of this first generation electrolyser with excellent performance in terms of overall efficiency, internal resistances and current–voltage response [4]. This development opens the door to the fabrication of light weight and cheap electrolysers as well as related electrochemical devices such as flow batteries and fuel cells. During the Phase II work, we explored the feasibility of using commercial desk-top printers to print bipolar plates for the fuel cell stacks.

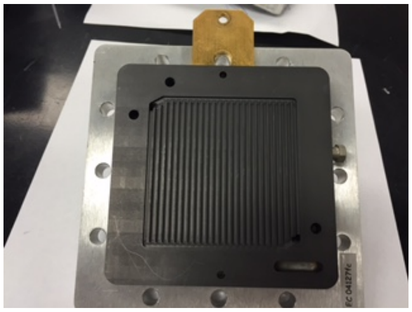


Fig.22. A flow plate for direct ethanol fuel cell stack.

As shown in Fig.22, a commercially available bipolar plate is used as a bench-mark design for the flow plate. Three types of 3D printers including stereolithography (SLA) 3D printer, an Objet30 Pro 3D printer and a fused filament deposition (FFD) 3D printer were available to print the bipolar plates, shown in Fig. 23. By comparing three parts produced from three different 3D printers, it seems that SLA printer produced the flow plates with the best resolution. All the parts shown in Fig. 23 were made of acrylonitrile butadiene styrene (ABS) polymers. All these three printers are not allowed to use customer’s materials, but must use their materials to print parts. Since the ABS is not an electric conductor, the flow plates needs to be coated with electric conductible materials. As shown in Fig.24, a thin layer of Au film was plated by a sputtering vapor deposition process on the surface of the bipolar plate printed by the FFD 3D printer. The adhesion of the coating was good, but the flow channels and some of corners were not completely coated. Further electrochemical deposition treatments are needed to achieve higher electric conductivity of the bipolar plates.


(a) (b) (c)

Fig.23. Flow plates fabricated by various 3D printers: (a) SLA-printer; (b) Objet30 Pro and (c) FFD-printer.

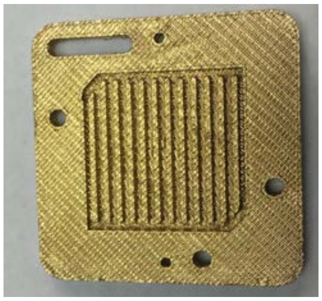


Fig.24. Au-plated bipolar plate printed by the FFD-printer.

SUMMARY

Through executing this SBIR II projects, we have successfully carried out our proposed work and developed some very promising key materials for direct ethanol fuel cell applications, which include MnO_2-based cathode catalysts for oxygen reduction reaction (ORR) and Pd-based anode catalysts for ethanol oxidation reaction (EOR). Furthermore, composite membranes with improved fuel crossover property were developed. The DEFCs using the new anode and cathode catalysts and membranes achieved peak power densities up to 150 mW cm^{-2} and 60% fuel energy efficiency by using optimal fuel compositions (2M ethanol and 3M KOH) at 90 °C, which is comparable with state-of-the-art PEM-DMFCs that utilize expensive Pt-based catalysts and proton exchange membranes, and high pressure oxygen gas. In order to successfully commercialize the AAEM-DEFC technology for potential markets to replace rechargeable Li-ion batteries, several major technology hurdles still need to be addressed, including (1) the EOR mainly proceeds via a 4-electron acetate pathway rather than 12-electron CO_2 pathway with the Pd-based anode catalysts; (2) fuel crossover from the anode to the cathode that results in flooded cathode and increased cathode overpotentials; (3) fuel cell design and fabrication methods yet to be further developed to improve system energy efficiency and reduce the manufacturing cost of the DEFC stacks and systems. Further development in the subsequent Phase II SBIR project will overcome these major technical challenges for DEFCs and to explore the transition/commercialization path of the developed products.

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INVITED LECTURES

1. R. Chen, “Electrocatalysis of Alcohol Oxidation Reactions on Pt and Pd Electrocatalysts in Alkaline Media”, *Energy Materials Nanotechnology Meeting on Electrocatalysis*, Orlando, Florida, Feb. 15-19 2016.
2. R. Chen, “Electrocatalysis of Oxygen Reduction Reaction and Ethanol Oxidation Reaction on Multifunctional Catalysts in Alkaline Media”, *Electrochemical Conference of Energy and Environment*, *E3*, Shanghai, China, March 13-16, 2014.
3. R. Chen, “Polymeric Electrolytes and Catalysts for Anion-Exchange-Membrane Fuel Cells”, *The 8th Pacific Rim International Congress on Advanced Materials and Processing (PRICM-8)*, Waikoloa, Hawaii, August 4-9, 2013.

PRESENTATIONS IN INTERNATIONAL CONFERENCES

1. R. Chen* and J. Guo, “Effects of Pb on Electrocatalysis of Alcohol Oxidation Reaction on Pt/C Catalysts in Alkaline Media”, *the 229th Electrochemical Society Meeting*, San Diego, California, May 29 – June 2, 2016.
2. R. Chen* and J. Guo, “Effects of Pb in Electrocatalysis of Ethanol Oxidation Reaction on Pd/C and PdRu/C Catalysts in Alkaline Media”, *the 229th Electrochemical Society Meeting*, San Diego, California, May 29 – June 2, 2016.
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