The focus of the first year of this two-year program was the development of an electrolyte system for fuel cells and other electrochemical reactors, which allows proton transfer through the electrolyte system but prevents crossover of larger chemical species from one electrode side to the other electrode side of the fuel cell. The first year effort of this program resulted in the filing of a U.S. patent application in Jan. 16, 1996 that was issued on Dec. 8, 1998 (United States Patent 5,846,669). The patent was based on work published in 1995 by Cong Pu, Wenhua Huang, K. L. Ley and E. S. Smotkin, “A Methanol Impermeable Proton Conducting Composite Electrolyte System,” J. Electrochem. Soc., 142, L119-L120 (1995). This work was attributed to the DARPA grant. The second year of the program was focused on the development of new anodes for direct methanol fuel cells. This work resulted in a second patent entitled “Single Phase Ternary Pt-Ru-Os Catalysts for Direct Oxidation Fuel Cells” (United States Patent 5,856,036). Ley et al. based this patent on a publication, “Methanol Oxidation on single-Phase Pt-Ru-Os Ternary Alloys,” J. Electrochem. Soc., 144, 1543-1548 (1997). This work was attributed to the DARPA grant.
Direct Methanol Fuel Cell Development
Final Technical Report for
Grant number: DAAH04-95-1-0330

(1) Foreword

The focus of the first year of this two-year program was the development of an electrolyte system for fuel cells and other electrochemical reactors, which allows proton transfer through the electrolyte system but prevents crossover of larger chemical species from one electrode to the other electrode side of the fuel cell. The first year effort of this program resulted in the filing of a U.S. patent application in Jan. 16, 1996 that was issued on Dec. 8, 1998 (United States Patent 5,846,669). The patent was based on work published in 1995 by Cong Pu, Wenhua Huang, K. L. Ley and E. S. Smotkin, “A Methanol Impermeable Proton Conducting Composite Electrolyte System,” J. Electrochem. Soc., 442, L119-L120 (1995). This work was attributed to the DARPA grant. The second year of the program was focused on the development of new anodes for direct methanol fuel cells. This work resulted in a second patent entitled “Single Phase Ternary Pt-Ru-Os Catalysts for Direct Oxidation Fuel Cells” (United States Patent 5,856,036). Ley et al. based this patent on a publication, “Methanol Oxidation on single-Phase Pt-Ru-Os Ternary Alloys,” J. Electrochem. Soc., 144, 1543-1548 (1997). This work was attributed to the DARPA grant.

(2) Statement of the problem studied

There are two major obstacles to the commercialization of direct methanol fuel cells: (1) the kinetics of methanol oxidation are sluggish and (2) methanol crossover from the anode to the cathode causes a mixed potential at the cathode.

The oxidation of methanol is a six-electron process that involves the formation of carbon monoxide (CO) as an intermediate. This carbon monoxide poisons the Pt surface. The development of superior catalysts for the oxidation of methanol requires consideration of the mechanism for methanol oxidation. Alloy catalysts have been studied for methanol oxidation and the consensus is that the “bifunctional theory” can be used to explain experimental data satisfactorily. Based upon this theory, the methanol electro-oxidation process can be described as follows:

\[ 
\begin{align*}
\text{Pt} + \text{CH}_3\text{OH} & \rightarrow \text{Pt-(CH}_3\text{OH)}_{\text{ads}} & (1) \\
\text{Pt-(CH}_3\text{OH)}_{\text{ads}} & \rightarrow \text{Pt-(CH}_3\text{O)}_{\text{ads}} + \text{H}^+ + e^- & (2a) \\
\text{Pt-(CH}_3\text{O)}_{\text{ads}} & \rightarrow \text{Pt-(CH}_2\text{O)}_{\text{ads}} + \text{H}^+ + e^- & (2b) \\
\text{Pt-(CH}_2\text{O)}_{\text{ads}} & \rightarrow \text{Pt-(CHO)}_{\text{ads}} + \text{H}^+ + e^- & (2c) \\
\text{Pt-(CHO)}_{\text{ads}} & \rightarrow \text{Pt-(CO)}_{\text{ads}} + \text{H}^+ - e^- & (2d) \\
\text{M} + \text{H}_2\text{O} & \rightarrow \text{M-(H}_2\text{O)}_{\text{ads}} & (3a) \\
\text{M-(H}_2\text{O)}_{\text{ads}} & \rightarrow \text{M-(OH)}_{\text{ads}} + \text{H}^+ + e^- & (3b)
\end{align*}
\]
Pt-(CO)$_{ad}$ + M-(H$_2$O)$_{ad}$ → Pt + M + CO$_2$ + 2H$^+$ + 2e$^-$  \hspace{1cm} (4a)
Pt-(CO)$_{ad}$ + M-(OH)$_{ad}$ → Pt + M + CO$_2$ + H$^+$ + 2e$^-$  \hspace{1cm} (4b)

Thus, good catalysts should have at least two metals, Pt and “M”. Pt is a good CH bond activator and the function of M to activate water. Water is required to provide the second atom of oxygen for conversion of CO to CO$_2$. The problem is to find optimum compositions for catalysts with the aim of lowering the activation energy for methanol oxidation within the potential window of direct methanol fuel cells.

Methanol crossover is another key obstacle to the commercialization of direct methanol fuel cells. Renegade methanol that crosses over from the anode to the cathode, is directly oxidized at the cathode by the oxygen. Electron transfer from renegade methanol to oxygen does not yield external circuit electrons. Further, crossover oxidation ties up valuable catalytic sites at the cathode and reduces overall fuel cell performance. The stoic ratio of air must be increased to accommodate the “crossover current”. In addition, the extra water formed by the direct oxidation of methanol, and the CO$_2$ formed both impede the mass transport of oxygen to the three phase interface at the cathode porous electrode. Since the permeability of methanol through the electrolyte increases as the temperature is increased, improvements at the anode side realized by increasing the temperature are lost at the cathode due to methanol crossover. The problem is to develop electrolyte composites, which do not permit methanol to crossover.

(3) Summary of the most important results.

The first year of the program focused on the methanol crossover problem. Pd foils were sandwiched between two sheets of Nafion and membrane electrode assemblies (MEAs) were prepared. These MEAs were tested in the hydrogen/air mode for proof of concept. Initially we used 25 micron thick Pd foils. Our initial results were poor. We could not pass any current through the Pd foil. We determined that the problem was surface activation of the foil. The roughness factor of the foil has to be increased. This was accomplished first by palladizing the surface of the Pd foil with Pd to increase the surface area. After this, the high surface area Pd was further activated by platinization of the Pd. This was required in order to effect cleavage of the H$_2$ bond. The exchange current for this process is much larger on Pt than it is on Pd. However, Pt is not permeable to hydrogen. This is why the surface area was increased using Pd black, but activated with Pt. Activation of the surface of the Pd was successful and the composite electrode permitted significant current in a hydrogen/air fuel cell and this was published in the Journal of the Electrochemical Society and patented. The methodology for activating the surface of Pd is now widely used by technologies requiring the purification of hydrogen. This technology could also be used for micro fuel cells employing hydrogen as a fuel.

Unfortunately, when the surface modified Pd foil was used in the direct methanol fuel cell mode, no current could pass. Further research revealed the following. In a hydrogen fuel cell, the high partial pressure of hydrogen causes the Pd to undergo a phase change. This phase change causes the Pd to go from the alpha phase to the beta phase. It is the beta phase that is permeable to the hydrogen. The alpha is not
permeable to hydrogen. In a direct methanol fuel cell, the partial pressure of hydrogen is too low to cause the phase change. Our group made a tremendous effort to put down very thin films of Pd onto the Nafion to reduce the resistance of the foil to hydrogen transport. We found that it is impossible to produce thin films that can tolerate the mechanical stresses created by assembly of a fuel cell. Theoretical calculations suggest that these foils will never be useful for direct methanol fuel cells although may have applications in fuel cells using very “dirty” hydrogen or hydrogen contaminated with methanol. The work published in JES demonstrated the use of the Pd foil while using hydrogen saturated with methanol. We demonstrated that methanol did not reduce performance of fuel cell contaminated with methanol when PtRu was used as the anode catalyst. This technology is now being developed by Manhattan Scientists towards the development of micro fuel cells.

The second year of the program focused on the development of ternary alloy catalysts for direct methanol fuel cells. We developed a rational approach to the design of catalysts that is based on metal oxygen and carbon bond energies, and phase equilibrium considerations. Briefly, the concept is that the alloying component should have metal oxygen bond energy similar to the Pt carbon bond energy. This is about 600 kJ/mole. We published a diagram showing all possible candidates in the Journal of the Electrochemical Society and have since followed up with papers in Science and the Journal of Physical Chemistry. In addition to bond energy considerations, phase equilibria is also considered. If the alloying component is not sufficiently soluble in the platinum fcc lattice, Ru is used as a diluent to solubilized the metal. Our first test case was PtRuOs. When the current densities of fuel cells using this catalyst are normalized to surface area, this catalyst has been shown to be better than PtRu. Recently Andrzej Wieckowski has reported data, which explains why Os is good and this data will be published soon. Professor Wieckowski is one of the ARO HUB subcontractors. It should be noted at this point that Debra Rollison of the NRL has confirmed that these binary and ternary alloys, have a much more complex structure and a simple alloy. In fact Rollison’s data suggests that an amorphous phase may play an important role in catalysis. Our results, recently published in the Journal of Physical Chemistry (Bogdan Gurau, Ramesh Viswanathan, Renxuan Liu, Tod J. Lafrenz, Kevin L. Ley, and E. S. Smotkin, “Structural and Electrochemical Characterization of Binary, Ternary, and Quaternary Platinum Alloy Catalysts for Methanol Electro-oxidation,” J. Phys. Chem. B, 102, 9997-10003. (1998)) show that a true alloy phase in one of several components in these mixed metal catalysts. Since our publications concerning ternary catalysts have come out, ternary catalysts have been the subject of numerous RFPs concerning fuel cell catalysts.

(4) List of all publications and technical reports


(5) List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project.
Renxuan Liu, PhD 1998
Li Liu, MS 1998

(6) Report of Inventions