V.B Hydrogen and Fuel Cell Demonstration/Analysis

V.B.1 Alkaline Fuel Cell-Battery Hybrid Systems with Ammonia or Methanol as Hydrogen Supply

Robert R. Aronsson (Primary Contact), Karl Kordesch, Martin Cifrain, Gerold Koscher, Gottfried Faleschini, Viktor Hacker
Apollo Energy Systems, Inc.
2301 NW 33rd Court
Pompano Beach, FL 33069
Phone: (954) 969-7755; Fax: (954) 969-7788; E-mail: electricauto@worldnet.att.net

DOE Technology Development Manager: Sig Gronich
Phone: (202) 586-1623; Fax: (202) 856-9811; E-mail: Sigmund.Gronich@ee.doe.gov

Objectives

Design an alkaline fuel cell system with circulating electrolyte for intermittent duty service and small units operating in a hybrid mode.

- Develop and optimize a low-cost ammonia cracker for supplying hydrogen as gas.
- Use liquid fuels like methanol or boro-hydrides in alkaline electrolytes.
- Replace the presently-used Pt catalysts if possible at cathodes and anodes.
- Demonstrate that these systems work like zinc-air cells with replaceable anodes.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Hydrogen Delivery

- F. Transport Storage Costs

Fuel Cells

- M. Fuel Processor System Integration And Efficiency
- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance

Approach

- Design fuel cell systems in the range of 100 W to 2.5 kW.
- Test the ammonia crackers and fuel cells in-house and in outside laboratories.
- Compare the use of ammonia crackers with direct alkaline methanol units.
- Analyze the results and check their compatibility in hybrid operation.
- Optimize the air-cleaning (CO_2-removal) methods for long-life applications.
- Check the disposal or regeneration possibilities of used alkaline electrolyte.

- Select low-cost, simple commercial accessories whenever possible.
- Select the necessary personnel for development and testing of electrochemical systems and application devices.

Accomplishments

- Several 250-kW alkaline fuel cells with circulating potassium hydroxide (KOH) electrolyte were built and tested at the Technical University of Graz (TUG) in Austria and at Apollo's laboratory in Fort Lauderdale, Florida. Results were excellent and the fuel cells were demonstrated to hundreds of persons in Florida over a period of four years.
- A 2.5-kW Apollo power plant, which included a lead-acid battery and DC to AC inverter, was built and demonstrated at the Florida Atlantic University in 2003.
- An ammonia cracker was developed and tested at the TUG and demonstrated at Apollo's laboratory in Florida over a four-year period. It provided an excellent and safe method of delivering hydrogen.
- The efficiency of conversion of ammonia to 75% hydrogen and 25% nitrogen was 99.9% at relatively low temperature (600°C) so that low-cost building materials can be used. Ammonia traces do not harm alkaline fuel cells.
- Several models in the ranges from 1 to 2.5 kW have been built. Very small crackers (100 W) are feasible with good heat insulation.
- Direct methanol fuel cells (DMFCs) with circulating electrolyte and methanol sensors have been built. It was proved that the cross leakage can be lowered by circulation in presence of a micro-porous separator allowing use of Pt-metal catalysts.
- However, the use of a silver catalyst was demonstrated as a very good replacement for a Pt catalyst, and no cross leak damage is noticed independent of the amount of methanol in the electrolyte. This way the units are very simple to build and to operate without expensive accessories.

Future Directions

- Evaluate the technical designs and prepare for future mass production of simple units in the 100-W to 2.5-kW size range.
- Analyze the cost advantages of different designs of ammonia crackers.
- Analyze the cost advantages of direct methanol cells with Ag catalyst.
- Conduct long-life and durability tests. Check the standing time of units which are used in interrupted service regimes.

Introduction and Approach

The revival and improvement of alkaline fuel cells with circulating KOH was started in 1997 at the Technical University of Graz in cooperation with Apollo Energy Systems, Inc. (AES). Thin carbon electrodes with new improvements can now deliver up to 400 mA/cm^2 on air [1]. After this revival of the alkaline fuel cell technology, it became necessary to answer questions about the advantages, lifetimes (aging mechanisms), cost of accessories, and estimates about competitive pricing with other fuel cell systems which use larger amounts of noble metal catalysts. The development of low-cost ammonia crackers followed. It became obvious that ammonia, which can also be produced from renewable sources, is well suited as a worldwide hydrogen source [2].

Alkaline direct methanol fuel cells were investigated to replace the acidic proton exchange membrane (PEM) DMFCs. This technology can very well compete with zinc-air batteries with replaceable anodes. This is especially true if a silver catalyst is used [3, 4].

A new laboratory for R&D on alkaline fuel cells and for the demonstration of complete fuel cell systems with H$_2$ fuel from ammonia crackers has

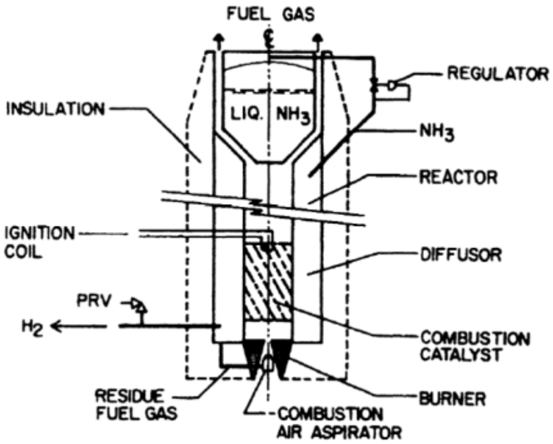

Figure 1. Principle of an Ammonia Cracker (Reference 1)

been leased in Pompano Beach, Florida. Test procedures with alkaline DMFCs and their hybrid operation with improved lead-acid batteries and a line of DC/AC inverters have now been established by Apollo Energy Systems, Inc.

Results

Ammonia has been identified as a suitable hydrogen carrier. Ammonia is essentially non-flammable and is readily obtained and handled in liquid form in low-pressure cylinders. Ammonia contains 1.7 times as much hydrogen as liquid hydrogen for a given volume. Ammonia is produced and distributed worldwide in millions of tons per year quantities. Procedures for safe handling have been developed in every country. Facilities for storage and transport by barges, trucks and pipelines from producer to ultimate consumer are available throughout the world. Therefore, liquid anhydrous ammonia is an excellent storage medium for hydrogen. The fuel capacity per weight of ammonia is higher than that of methanol, and the price per kWh is lower. Ammonia can be cracked into hydrogen and nitrogen in a suitable unit according to the reaction: $2\ NH_3 \Rightarrow 3\ H_2 + N_2$ (see Figures 1, 2, and 3). With ammonia there is no shift converter, selective oxidizer or further co-reactant like water required as in other hydrocarbon or alcohol fuel cell power devices. The generated nitrogen can be released to the atmosphere without significant environmental impact. The dissociation rate depends on temperature, pressure and type of catalysts. Pointing to the future use of hydrogen from ammonia cracking, it should be mentioned that the alkaline fuel cell is insensitive to any amount of NH_3. Acidic PEM fuel cells can use hydrogen from ammonia

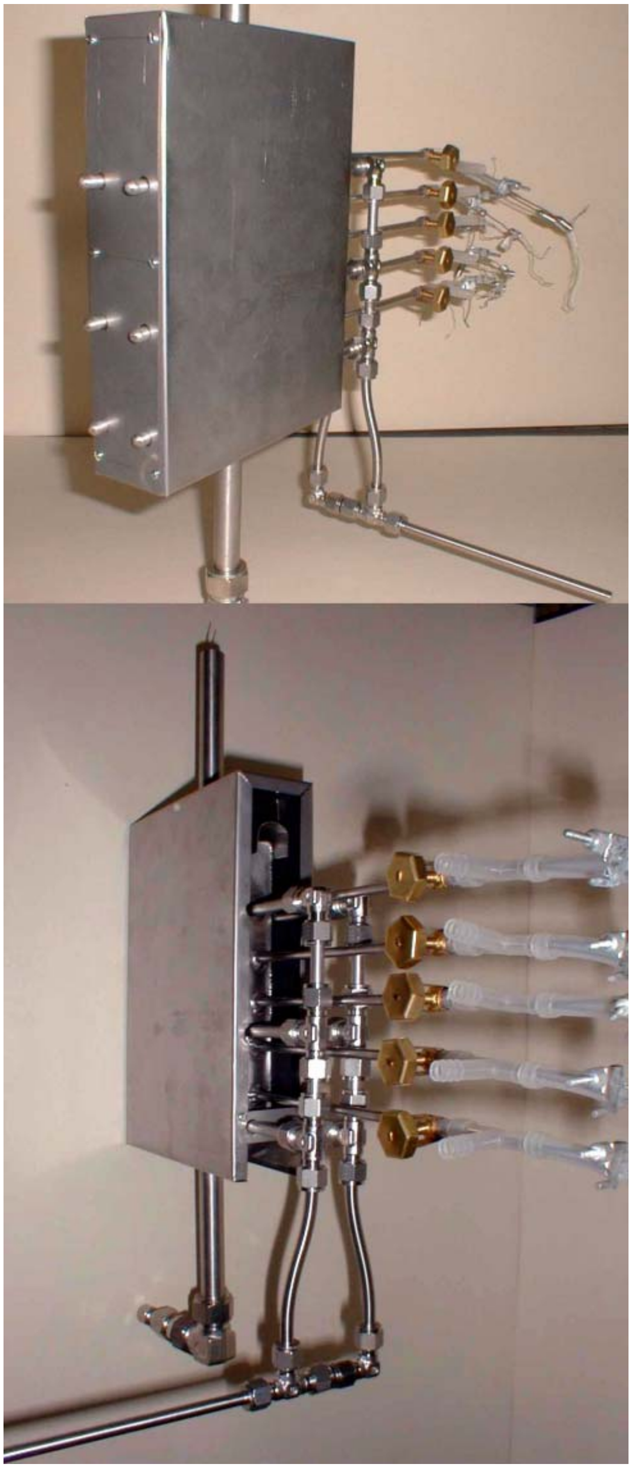

Figure 2. Plate-type Ammonia Cracker for Alkaline Fuel Cell Applications, without Heat Insulation, Front And Rear View

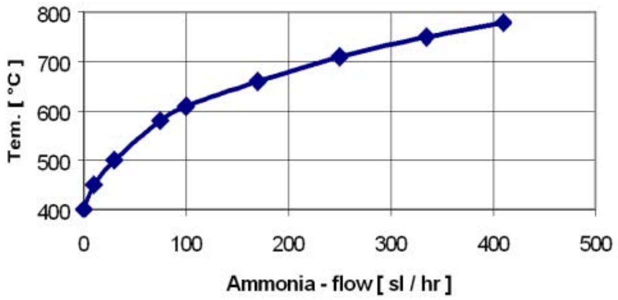

Figure 3. Cracking Efficiency (>99.99% conversion) 20 g Ni-based Ru Catalyst (suitable also for PEMs)

Figure 4. The TU-Graz/Apollo Alkaline Fuel Cell/Hybrid System with Ammonia Cracker (in the rear, heat-insulated)

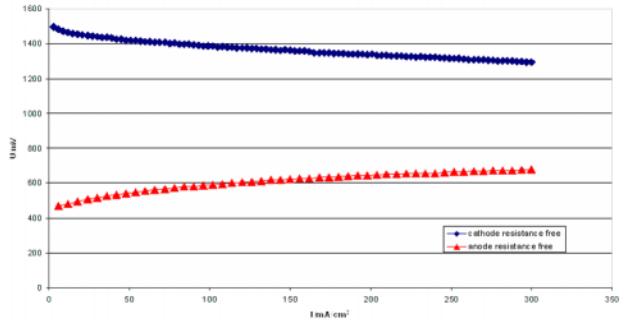

Figure 5. Methanol-Air Cell with Ag Catalyst and Newly Designed Anode. No sensitivity to methanol concentration in flowing electrolyte. Range: 0-300 mA/cm^2. Reference: Zn 1.5 V, Res. Free Voltage

crackers (see Figure 4), but the small traces of ammonia must be removed.

Alkaline methanol-air cells which use new types of Ag catalysts (Patent Application) showed that there is no reaction with methanol on the cathode and that the methanol can be added directly to the circulating electrolyte. After use, an exchange of the carbonated electrolyte can be accomplished by refilling with a methanol-KOH mix. The air electrodes remain unchanged. The KOH is the means for thermal management and CO_2 removal. The cells can be used like Zn-air cells with mechanically exchangeable anodes, with the advantage that the carbonated electrolyte can be discarded and a new methanol-alkaline electrolyte mixture can be refilled.

Anodes: The starting point in anode development was the three-phase anode as it is used in the alkaline fuel cell. It was a typical gas diffusion electrode with a diffusion layer and an active layer. An expanded metal was used as the current collector. Improvements: changing the binder resulted in better performance, but changing the structure to a two-phase flow electrode resulted in the best performance. A new nickel foam structure was used as the current collector.

Cathodes: As with anodes, the starting point of the development of cathodes was the common alkaline fuel cell cathode. Tests with Pt-metal catalysts showed us that the methanol crossover causes a drastic drop of the potential of the cathode. Using a membrane and circulating the electrolyte can minimize this problem, but using a catalyst which cannot oxidize the methanol is definitely the better way. In alkaline solutions, the use of silver for the oxygen reduction is recommended. The experiments made with cathodes with silver as catalyst showed clearly that there is no influence of methanol on the catalyst, even at high methanol contents. The amount of silver catalyst ranges from 1 to 5 mg/cm^2 and is very low (Figure 5) when compared with older work (by Siemens).

Conclusions

In order to continue this very successful experimental work, the necessary personnel will be hired, including chemists for cell testing, technologists for system modeling, and design and electronic engineers for controls.

References

1. "Fuel Cells and their Applications", by K. Kordesch and G. Simader, VCH Weinheim / Wiley, 1996, Chapter 8.13.1 Ammonia, Chapters 4.7 & 4.8 Methanol and Air Cells.

2. P.N. Ross Jr., "Characteristics of an NH_3-Air Fuel Cell System for Vehicular Applications", Proc. 16th Intersoc. Eng. Conf. 1981, pp. 726-733.

3. I.W. Kaye, D.P. Bloomfield, "Portable Ammonia Powered Fuel Cell", Power Sources Conf., Cherry Hill, pp. 408-809, 1998.

4. G. Faleschini, V. Hacker, M. Muhr, K. Kordesch, R.R. Aronsson, "Ammonia for High Density Hydrogen Storage", Fuel Cell Seminar, October 30-November 2, 2000, Portland, Oregon, abstracts pp. 336-339.

FY 2003/2004 Publications/Presentations

1. K. Kordesch, V. Hacker, G. Faleschini, G. Koscher, M.Cifrain, Ammonia as Hydrogen Source for an Alkaline Fuel Cell–Battery Hybrid System, Fuel Cell Seminar 2003, Miami Beach, November 3-6, 2003.

2. R.R. Aronsson et al. (Apollo Energy System Inc.), Uninterrupted Power Source, in: US-DOE-Annual Progress Report FY 2003, V. 11, pp. 41-43.

3. G. Koscher and K. Kordesch, Can Refillable Alkaline Methanol-Air Systems Replace Metal-Air Cells at the 23rd International Power Sources Symposium, Amsterdam, September 22-24, 2003.

4. G. Koscher and K. Kordesch, Alkaline Methanol-Air System, Journal of Solid State Electrochem. (2003) 7: 632-636.

5. Six papers published in the Handbook on Fuel Cells, Fundamentals. Technologies and Applications (ISBN: 0-471-49926-9) by J. Wiley & S. Ltd, Chichester, UK, 2003.

6. K. Kordesch, M. Cifrain, G. Koscher, V. Hacker, T. Hejze, R.R. Aronsson, A Survey of Fuel Cell Systems with Circulating Electrolytes, 41st Power Sources Conference, Philadelphia, June 14-17, 2004.

Patent Applications

1. Alkaline Fuel Cells: Electrode Structures, Catalysts: K. Kordesch, M. Cifrain

2. Ammonia Crackers: G. Faleschini, V. Hacker, K. Kordesch

3. Additives to Gas Supply of Fuel Cells

4. Tripolar Lead-Cobalt Batteries, R.R. Aronsson

5. Method For Producing Lead Foam

6. Alternative Method for Producing Lead Foam