



2301 NW 33rd Court, Bldg 115 Pompano Beach, FL 33069 Tel: (954) 969-7755 Fax: (954) 969-7788 Email: electricauto@att.net Web: http://www.apolloenergysystems.com



2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review Presentation

Alkaline Fuel Cell -Battery Hybrid Systems with Ammonia or Methanol as H₂- Supply

Apollo Energy Systems, Inc., Pompano Beach, FL, 33069 electricauto@worldnet.att.net April 23, 2004

This presentation does not contain any proprietary information.

Objectives

- Design of an Alkaline Fuel Cell System with circulating Electrolyte for vehicles in intermittent duty service and small units for uninterruptible hybrid power supplies.
- Development of low cost Ammonia Cracker
- Optimization of System Performance & Life
- Cost Reductions for accessories, especially:
- Pt-Catalyst reduction, use of Silver catalyst

Budget

QUARTERLY PROGRESS REPORT TO THE FLORIDA ENERGY OFFICE

Department of Community Affairs

Contract 03-SE-84-11-16-12-440

Uninterrupted Power Source DE-FG-44-02R410856

<u>1st Quarter 2004 - January 1 – March 30, 2004</u>

FINANCIAL STATUS

The total budgeted amount is \$140,000 grant, on a cost reimbursement basis, with \$140,000 of matching funds required, for a total of \$280,000 to be spent on the project. The anticipated project duration is 24-months.

<u>Total expenditure</u> to date has been \$140,000 <u>excluding</u> matching funds

Grant balance is \$ -0- as shown below:

Grant <u>\$140,000.00 – paid</u>

Matching Funds <u>\$140,000 – paid</u>

Technical Barriers and AFC-Targets

- Cost of Components: commercially purchased
- Stack Material: Carbon Electrodes on metal screens
- H₂-Catalysts: Low Pt-level (below 0.5 mg/cm2)
- Air-Catalyst: Non Noble Metal, low-level Silver Catalyst
- Durability: 5000 hours intermittent duty (for a vehicle)
- Cell Performance: 150-300 mA / cm^2 at 0.8V, 80 °C
- Thermal & Water Mgmt.: circulating electrolyte
- Stack Cost: in Mass Production: \$35–50/kW
- Fuel Cost: Compare: NH₃: \$ 1.17 / kWh, Methanol: \$ 3.79 / kWh, H₂: up to \$ 25 / kWh [Kaye, Bloomfield]

Problems

- New Energy Technologies like Fuel Cells and Fuel Cell Hybrids need Hydrogen
- The Handling and Storage of Hydrogen is questionable, dangerous and expensive
- Can Ammonia as Global Hydrogen Carrier solve the Storage and Distribution Situation
- What other H₂ Carriers are to consider ?
- Are renewable Energy Sources like water, wind, thermal, nuclear, Bio-technology, available at reasonable cost?

Reformer Gas with 10 to $15 \% CO_2$ cannot be used in AFCs because:

$2 \text{ KOH} + \text{CO}_2 \rightarrow (2\text{K}^+ + \text{CO}_3^{2-}) + \text{H}_2\text{O}$

- \odot increasing viscosity, hence reduced diffusion rates
- $\ensuremath{\mathfrak{S}}$ reduction of O_2 -solubility, hence activation loss on cathode
- ⊗ carbonate salts are less soluble and might precipitate
- ⊗ electrolyte conductivity is reduced, hence higher losses
- ☺ For CO_2 cleaning from air (0.03 % CO_2) a simple Sodalime scrubber can be used

Further Develop the Advantages of the AFC

- low cost electrodes
- simple way of stack construction
- higher voltages
- sufficient lifetime for electric vehicles
- low sensitivity to misuse
- low sensitivity to impurities like CO or NH₃
- not sensitive to long periods of shutdown
- fast startup when used in hybrid mode

Advantages of Circulating Liquid Electrolyte

- easy thermal management
- easy water management
- barrier against reactant gas leakage established
- accumulated impurities and carbonate easily removable
- reduction of concentration gradient
- some parasitic currents (in multi cell stacks)

Advantages of Ammonia

- Simple Storage as Liquid
- High Storage Density at low Pressure
- Does not burn easily, No CO₂ No NO_x
- Easy and efficient to Crack (reform)
- Great Experience in Industry and Farming
- Biologically completely safe if spilled in ground
- Lower Cost than Hydrogen or Methanol
- Strong smell indicates leakage

The Safety Aspects of Alkaline Fuel Cell Hybrids operated on H₂ from an Ammonia Cracker and Air

- The system does not use highly pressurized or volatile liquid hydrogen
- Ammonia is liquid at low pressure, not explosive and not flammable
- The Ammonia technology is globally distributed, NH_3 is in daily use, it is now produces from CH_4 but can be made from renewable sources.
- A medium temperature very efficient cracker made from stainless steel produces 75 % clean $H_2 + 25$ % N_2 without noble metal catalysts.
- If NH₃-gas escapes, it is a warning of leakage, irritations are reversible.
- Spilled liquid NH₃ is safe in the ground, spilled KOH carbonizes fast.
- AFCs with circulating KOH can be shut down completely over night. (no H_2 is left in unit) and started quickly in intermittent use patterns.
- **Observations:** The operation of an AFC in Hybrid Mode prevents dangerous cell reversals and guarantees quick and safe start-ups.
- An alkaline Fuel Cell operated City Car has been operated as Hybrid with a Lead-acid Battery in public traffic for 3 years by Karl Kordesch.

The Dangers of AFCs with Circulating Electrolytes

- KOH Electrolyte (7 to 12 N) is very corrosive
- Wash eyes with water or Boric acid immediately
- If spilled, it can be soaked up with sand, etc., and any mix will carbonate on air in a short time
- As Technical Product it is also used Commercially
- The fuel cells liquid manifolds are not pressurized
- Short Circuits may produce DC-arcing
- Shut-down systems are completely safe (no H_2)

Project Milestones

Uninterrupted Power Source

DE-FG-44-02R410856

1st Quarter 2004 - January 1 – March 30, 2004

Measurable Objectives

A number of tasks will have to be performed before the system is finally ready for delivery to the Department of Energy. The main tasks are shown below:

Milestones

	Task	Scheduled Completion	Progress To Date
1	Test 250-watt Apollo Power Plant in Company lab	November 2002	Complete
2	Test 2.4 kW power plant in customer laboratory	December 2002	Complete
3	Study Advanced DC to AC Inverters	March 2003	Complete
4	Study available Power Plant-to-Grid Switches	March 2003	In Progress
5	Study available Hydrogen Sensors	March 2003	Complete
6	Sub-contract battery production to USA company	September 2003	Complete
7	Design microprocessor logic system	September 2003	In Progress
8	Test 2.5 kW Apollo Power Plant at Cologne plant	September 2003	Complete
9	Build new 5 kW Apollo Power Plant in Cologne	March 2004	Complete
10	Test new 5 kW Apollo Power Plant at Fla. Tech. Center	September 2004	
11	Deliver 5 kW Apollo Power Plant to US DOE	September 2004	

Properties of Apollo-Electrodes



Fuel Cell Running on Ammonia





Anhydrous Ammonia Ammonia Cracker

Fuel Cell Module II

Hybrid battery (lead acid) Electric Motor and Fan

Sufficient Lifetime for an Electric Vehicle

<u>Given</u>: Total Range of a vehicle: 200.000 km

Medium velocity:

Therefore, the operating time is

~ 4000 hours

50 km/hr

- **IF**: **I** liquid circulating electrolyte is used
 - ➡ electrolyte leaves the cell after shutdown

Lifetime of an AFC-electrode:

~ 4000 hours

NO MORE LIFETIME THAN 4000 OPERATION HOURS IS NECESSARY FOR MOBILE APPLICATIONS

CO_2 – Removal with Soda lime

- Air contains 0.03 percent or 300 ppm of CO_2
- * 1kg Sodalime absorbs up to 15 wt. percent, i.e., 150g CO_2 from 25m³ properly humidified air
- I kg Sodalime could completely clean 25m³ Air, which theoretically contains the oxygen needed to operate a 1 kWh Alkaline FC for 200 Hours
- If the air supplied is used only with circa 50 % efficiency (1/2 x stoichiometric) the practical service time from 1 kg Sodalime is estimated to be about 100 hours for a 1 kW alkaline FC

Silver Catalysts instead of Pt

- Alkaline fuel cells and Air Cells can replace the cathodic catalysts with silver at about 1/100 of the cost. Porous Metals or Carbons can be carriers.
- The high performance is similar to the Pt-metals
- The up to now problematic life time is controllable by certain Ag-catalyst preparations (Pat. Appl.for).
- The fuel cells with Ag catalysts are especially well suitable for Battery Hybrid Systems used in on-off applications if cell reversal is prevented
- If considered useful, carbonate precipitation traps can be installed in circulating electrolyte systems.

Small Portable Direct Alkaline CH₃OH-Fuel Cells

- Progress in Development of small units:
- 1992: 25 mW/cm², 2003: 65 mWh/cm²
 25 mA/cm², 100mA/cm²
- Anode with PTFE-Binder
- Cathode with Ag-Catalyst, no cross leakage
- Unlimited Storage with separate KOH & Methanol Filler, re-fillable and re-usable

Alkaline Methanol-Air Fuel cells with circulating electrolyte.

- Primary methanol-air cells are filled once
- Systems with circulating electrolyte are filled with new methanol, dependent on the signals from a methanol sensor so that the concentration stays at the optimum level. (Sensor: patent applied for).
- A membrane (a layer of a low-cost microporous separator type) lowers any cross-leak situation in case of the use of Pt-metal cathode catalysts.
- Cathodes with Ag-catalyst, spinells or perovskites are insensitive to methanol cross-over

Interactions and Collaborations

- In 1997 Apollo engaged the Technical University of Graz, Austria (TUG) to revive the Alkaline Fuel Cell (AFC) which Dr. Karl Kordesch had developed while working as a scientist at Union Carbide in the 1960s and 1970s. Another task for TUG was to take the cost out of the AFC. Dr. Kordesch headed up the project from 1997 to the present time. Research and development has progressed steadily on the project with up to 15 professors and graduate students engaged in the effort. Besides improving the AFC and taking cost out of it, an Ammonia Cracker was developed and several prototypes made.
- Based on this work, three patent applications have been made and assigned to Apollo Energy Systems, Inc. At present, a Silver catalyst (to replace platinum) and a Direct Methanol Alkaline Fuel (DMAFC) are under development.