DGP-WG/05-IP/2
(related to DGP-WG/05-WP/22)
14/3/05

DANGEROUS GOODS PANEL (DGP)

MEETING OF THE WORKING GROUP OF THE WHOLE

Montreal, 18 to 22 April 2005

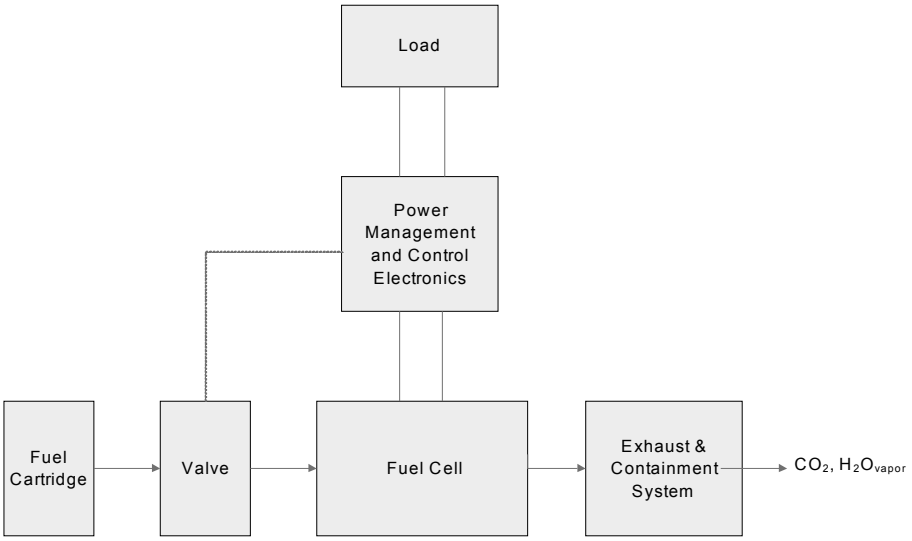
Agenda Item 2: Development of recommendations for amendments to the *Technical Instructions* for incorporation in the 2007/2008 edition
2.8: Part 8 - Provisions Concerning Passengers and Crew

FORMIC ACID FUEL CELL SYSTEMS

(Presented by Judith Code)

Formic Acid Fuel Cell System Block Diagram

As shown in the block diagram below, the major components of a FAFC system are the fuel cell, a formic acid fuel cartridge, the fuel flow valves, the power management and control electronics and the by-products exhaust and containment systems.

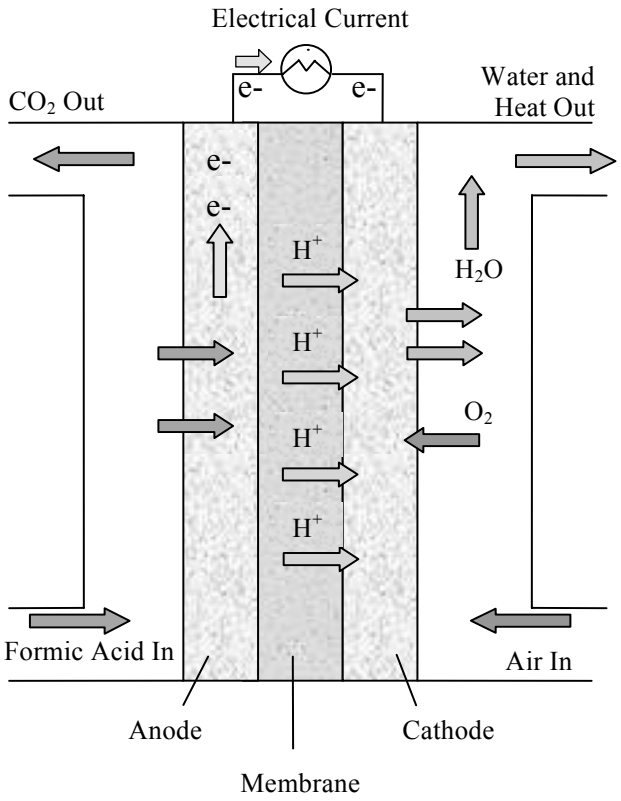


SIMPLE BLOCK DIAGRAM FOR
FORMIC ACID FUEL CELL SYSTEM

Fuel Cell Chemical Reaction

A FAFC System is a PEM (proton exchange membrane) fuel cell where the formic acid, in the presence of a catalyst, is chemically split into protons, electrons and carbon dioxide at the anode. The protons diffuse through the PEM membrane to the cathode side where it combines with oxygen from the air and the electrons returning from the load, in the presence of a catalyst, to form water. The figure below shows a diagrammatic view of how a FAFC works.

FAFC Diagram



The chemical equations below summarize the reactions at the anode and cathode.

Anode: $HCOOH \rightarrow 2H^+ + 2e^- + CO_2$
Cathode: $2H^+ + \frac{1}{2} O_2 + 2e^- \rightarrow H_20$

The complete chemical equation of the reactions that occur in the FAFC system is as follows:

$HCOOH + 1/2O_2 \rightarrow H_2O + CO_2$

Note: In the above equations the fuel is converted into electricity through an electro-chemical process, it is not combusted.

Physical and Functional Description

The FAFC power systems discussed in this document will have the following specifications:

- Fuel cell power output: # 20 watts
- Cartridge size: # 100 ml of fuel

- Fuel (formic acid) concentration: < 85% wt.
- Physical size: compatible with use in handheld devices

The photograph below shows a formic acid fuel cartridge designed and built for one of the FAFC systems. This particular one has a fuel capacity of approximately 50 milliliters.



Risk/Safety Analysis

A risk/safety analysis performed on the FAFC system recommended various product design controls and testing/qualification (risk mitigations) activities to eliminate safety critical failures and unacceptable risks. The table below summarizes those risks and risk mitigations (the design controls and test/qualification protocols) that will be implemented to achieve a safe product for the duration of the product life. In the table below, the numbers in the brackets in front of the items in the "Risk Mitigations" column indicates connections of that line item to the numbered items in the "Risk Description" column.

#	Risk Description	Risk Mitigations
1	**Formic acid (FA) leaks** out of cartridge from exposure to: **1.** **High temperature** (85°C) for 24 hours, **2.** **Low temperature** (-40°C) for 24 hours **3.** **Temperature cycling** (75°C for 2 hours, followed by -40°C for 2 hours, repeat above ten times with less than 30 minutes interval between temperature extremes) **4.** **Altitude change** in aircraft transportation (equivalent to 100 kPa for 6 hours @ 20°C) **5.** **Vibration** (sinusoidal 7Hz - 200Hz, 1gn -8gn) **6.** **Dropping** (from 1.5 m height as per transportation requirements and instructions) **7.** **Crushing** of cartridge (100 kg mass) **8**. **Cartridge components/material degradation** failure during life time of the product leading to: - personal injury from ingestion (toxic & corrosive), skin/tissue damage from contact (corrosive & toxic) - damage to equipment or carrier (corrosive, but due to small amounts in the cartridges # 100 ml, severity of damage should be low.)	C (1,4) The fuel cartridge will be designed and tested for excess over pressure withstand capability (caused by high temperatures and altitude change in aircraft of 100kPa + vapor pressure of fuel). C (1,2,3) The fuel cartridge will be designed to withstand extreme temperatures (- 40 and 85°C) and temperature cycling without leaking fuel and will be tested by a third party laboratory for verification of compliance. C (1,4) The fuel cartridge will be designed to relieve excess pressure in gases (CO) at the maximum operating design pressure level of the cartridge. C (5,6,7) The fuel cell cartridge will be designed to meet normal use and reasonable abuse vibration, drop and crush test specifications. C (8) Fuel cartridge components/materials which are in direct contact with formic acid will be checked and tested for suitability for use with formic acid over the life of the product. C (1,2,3,4,5,6,7,8) The FAFC system will be safety certified to the IEC Micro fuel cell standard which explicitly calls for extreme temperatures, temperature cycling, altitude change, vibration, drop, crush and critical components material qualification and compatibility with fuel tests. C Labels will be placed on the product with accompanying literature, warning against FA ingestion, contact, and exposure of cartridge to elevated temperatures over 85°C (e.g., open fire.) C **<u>Note:</u>** Formic acid has a pungent, unpleasant smell that repels more than attracts. This in itself will limit the amount that is ingested thus reducing the severity of effect.

#	Risk Description	Risk Mitigations
2	**Formic acid leaks** out from other FAFC system components that carry formic acid fuel, such as valves, tubes and the fuel cell when subjected to the tests and conditions outlined in 1 above.	C The risk mitigations and tests outlined for the fuel cartridge will apply to other fuel carrying system components also as deemed applicable to qualify other system components.
3	**1.** **Child gains access** to the formic acid inside the cartridge or the fuel cell system and ingests the fuel. **2.** FAFC System (cartridge and fuel cell power unit) can sustain **damage under reasonable consumer use and abuse** situations such that the fuel can leak or be accessed. leading to: - personal injury from ingestion (toxic & corrosive), skin/tissue damage from contact (corrosive & toxic)	C (1) Cartridge and fuel cell system components will be designed and tested to meet child resistant criteria. C (1,2) Product will be safety certified to the IEC Micro fuel cell standard which is a consumer based safety standard. The committee developing the standard has made all efforts to ensure all anticipated use and reasonable abuse conditions are mentioned in the standard. The standard references many other consumer product safety standards, such as safety standards for consumer information technology products. The standard also explicitly calls for the child resistant requirement. C (1,2) Cartridge and fuel cell system will be designed to ensure no leak occurs as per the risk mitigations mentioned in 1 above. C (1,2) The FAFC system will be designed tamper proof, such that without special tools (e.g., screw driver, metal knife, hammer) the system cannot be taken apart and the fuel accessed.
4	**Formic acid igniting** and catching fire leading to: causing personal and property damage	C Testing done in our labs showed that FA (concentrations to 94% wt.) is very difficult to ignite and does not sustain a fire. C FA (below 85% wt) from the most recent recommendations to UN is considered non-flammable. C FAFC systems under this ICAO proposal will use formic acid concentrations below 85% wt.

#	Risk Description	Risk Mitigations
5	**Carbon-monoxide emissions** from formic acid decomposition, may pose a CO poisoning danger to the passengers inside an aircraft cabin. OSHA Exposure limits are 25 ppm TWA and 200 ppm STEL. leading to: personal injury	C FA (94% wt.) decomposes into CO at a rate of 250cc/liter/75 days at 40°C. This equates to 0.167 ml of CO/100 ml fuel cartridge during a 12 hr flight. C FAFC systems will use FA (below 85% wt) that decomposes at a much slower rate than 94% FA. C Considering the lowest volume per passenger allocation in aircrafts ($1m^3$/passenger) and assuming no addition of fresh air (100% recirculation case), we get a CO concentration of **0.167 ppm** over 12 hours**.** Since TWA = 25 ppm for CO, **no CO buildup risk exists with 100 ml cartridges.** Note that this analysis is based on 94% wt formic acid and FAFC will use FA below 85% wt. C 150 cartridges per passenger, each producing CO at the above rates, will challenge the TWA of 25 ppm.
6	**Formic acid vapor emissions** challenges allowable exposure limits, caused by failure of FA vapor emissions control/containment system, leading to: people exposure (inhalation) of formic acid that challenges **5 ppm** TWA or 10 ppm STEL.	C FA vapor emissions control/containment will be designed with sufficient margin and robustness to ensure nominal performance over product life. C Life time and robustness testing will be done to qualify the design. C Emissions from the FAFC for all possible effluents will be tested appropriately. The IEC micro fuel safety standard explicitly calls for these measurements also. C **Note**: In the lowest volume per passenger allocation in aircrafts ($1\ m^3$/passenger) discussed earlier, with 100 % recirculation, **5 ml** of liquid FA can be vaporized and released by each of the FAFC fuel cell systems and the 5 ppm TWA level will not be challenged. This assumes one system per person.

#	Risk Description	Risk Mitigations
7	**Carbon-dioxide (CO_2)** emissions during operation challenges the **comfort level** in the passenger cabins of aircraft. Note: OSHA allowable exposure limits for CO_2 is 5000 ppm TWA and 30,000 ppm STEL.	C CO_2 emissions will be quantified over the product lifetime and its effects on the TWA exposure limits and the aircraft comfort level evaluated. C CO_2 emissions will be evaluated as per emissions testing section of IEC micro fuel cell safety standard. C Labels will be placed on the product and wording included in accompanying literature, instructing the user of the CO_2 emissions and recommending use in well ventilated areas or CO_2 monitored and controlled areas. **Note:** A 13 Watt FAFC system's CO_2 emissions is equivalent to an average human adult's (70 kg, sitting at rest) respiration rate.
8	Formic acid produces **Hydrogen (H_2) gas** at temperatures above 150°C or at lower temperatures but in the presence of a catalyst (as is the case during operation or possible fuel cell failure situations). leading to: - personal injury or equipment loss from hydrogen fire or explosion.	C In the lowest volume per passenger allocation in aircrafts (1 m^3/passenger), over 12 hours, with 100% recirculation, a buildup of H_2 to 25% of LFL (1% H_2 by volume in 1 m^3) allows a H_2 emissions rate of **14 ml/min** per FAFC system. Design will meet and exceed this specification for all conditions of operation. This will ensure no H_2 buildup can occur. C Pure hydrogen exhausted at 3 ml/min, from a hole that is mechanically not a flame quencher and in ideal wind conditions, will result in a standing flame. Design will be done and qualified to ensure that under all conditions, the hydrogen generated and exhausted is less than 3 ml/min. Since the hydrogen emission is mixed with CO_2 exhaust, a standing flame will not be possible at the exit. C FAFC uses a PEM membrane which allows the use of any hydrogen produced to generate electricity. C IEC Micro Fuel Cell Safety standard calls for hydrogen emissions testing also.

#	Risk Description	Risk Mitigations
9	Formic acid produces **Formaldehyde** at temperatures above 300ºC. leading to: - personal injury from exposure to formaldehyde	C Under normal operating conditions, average temperatures seen in the fuel cell will be 10 to 30ºC above room temperature. C Temperature sensors in the fuel cell will abort fuel cell operation if temperature runaway events were to occur. C The FA containment system will contain any transient formaldehyde formation internally. C IEC Micro Fuel Cell Safety standard calls for emissions testing of effluents.
10	Operation of the FAFC system may cause **oxygen depletion** to below 18% levels (considered unsafe threshold for humans) and challenges the comfort levels in passenger cabins in aircraft. leading to: Personal injury in terms of oxygen depletion.	C **Note:** In the FAFC system, O_2 depletion and CO_2 emission hazards are directly related to each other from the pure chemical reaction point of view. **$HCOOH + 1/2O_2 \rightarrow H_20 + CO_2$** C From the equation, O_2 consumption is at half the rate of CO_2 production. Since the O_2 level has to fall from 20.9% to 18% (a 3% drop) and the CO_2 has to rise to 0.5% (a 0.5% rise), the CO_2 problem will occur first. This makes the CO_2 production a more prevalent problem in the aircraft cabin than the O_2 depletion. C If adequate ventilation exists and the CO_2 level is at acceptable levels, then the O_2 depletion will not be an issue. C **Note:** A 13 Watt FAFC system's O_2 consumption is equivalent to one third (1/3) an human adult's (70 kg, sitting at rest) O_2 consumption rate. C Labels will be placed on the product or included in accompanying literature, instructing the user that the system consumes oxygen while in operation and that device should be used in adequately ventilated areas.

#	Risk Description	Risk Mitigations
11	**Product flammability hazard** - materials coupled with fuel vapor production, ignition sources, and electrical heat may cause fires.	C Materials of components which are in direct contact with FA will not support a flame. C FA concentrations of 84% wt and less are not flammable. Note: FAFC system will use FA concentrations of 84% wt or less. C Auto ignition temperature of pure FA is 539ºC. C All electronics in the fuel cell system will be non- arcing and non-sparking. C Control system monitors current draw and will trigger system shut down on an over-current situation. C Response of system to short circuit testing will be verified. C IEC standard calls for short circuit testing and checks for flammability rating of materials. C Labels will be placed on the product or included with accompanying literature, warning against exposing FAFC system to open fire.
12	**Long term storage** of system (fuel cell power unit and fuel cartridge) or cartridge only at elevated temperatures (60ºC) can lead to **buildup of CO** in confined air tight spaces leading to: personal injury from exposure to CO.	C Labels will be placed on the product or included with accompanying literature, warning against storage in confined spaces and at elevated temperatures for long periods of time. C Instructions will be included in accompanying literature advising that packaging of bulk quantities of cartridges or systems should be done in non air tight packages. C Carbon monoxide emissions risk mitigations, mentioned in risk # 5 earlier, apply here also.

Design Safety Features

The risk/safety analysis section, described above, shows the level of due diligence that the FAFC systems developers are committing to. This will ensure that consumer products released into the market place are safe. The following section summarizes the design safety features of the FAFC system.

Fuel Features

The fuel used in FAFC systems is less than 85% by weight concentration formic acid. This makes the fuel non-flammable (flashpoint > 65ºC) and less susceptible to CO decomposition. Also, formic acid has a strong pungent smell thus making it very unattractive to ingest or to come in contact with when leaked.

Fuel Cartridge Features

The fuel cartridge size is limited to 100 milliliters. This ensures access is limited to a restricted quantity of formic acid in case of exposure of cartridge to conditions above design and test specifications. The cartridge is designed to extremely stringent specifications of temperature, differential pressure, vibration, drop, crush, childproof, tamper proof, and material compatibility to fuel to ensure no leakage occurs in all foreseeable use and reasonable abuse scenarios. The cartridge is built out of a material that will ensure all safety measures are achieved. The connector will only allow fuel flow when mated with the proper mating connector as is the case when connected to the fuel cell power unit. Upon disconnecting the cartridge from the fuel cell power unit, the connector seals shut and stops fuel flow immediately.

Fuel Cell Power Unit Features

The fuel cell power unit will be designed to the same stringent requirements as the cartridge and will be tested similarly. The fuel that is present in the fuel cell power unit during operation is less than 10 milliliters and after shutdown the residual fuel is less than ten percent of that amount.

FAFC System Features

The FAFC system is designed with smart control electronics that monitor the FAFC system parameters and will trigger system shutdown (via shutting flow of fuel to the fuel cell power unit) when safety critical failures, such as high temperature, excess current draw, and unrecoverable voltage drop, occurs. This will ensure the termination of failures, e.g., large loads or internal short-circuits in the power control system, in the initial stages such that fires and extremely high temperature hazards do not occur. The control electronic will be designed and tested to consumer electronics levels of electromagnetic compatibility (EMC) specifications to ensure reliable operation of the safety control systems. Where applicable, appropriate component certification activity will be linked to the control system validation and qualification.

Effluents Containment and Controls

The FAFC system during operation, both in normal and abnormal conditions, may produce gas effluents such as carbon dioxide, carbon monoxide, formic acid, formaldehyde and hydrogen. Apart from carbon dioxide emissions risks, risks associated with the last four effluents (CO, FA, formaldehyde, and hydrogen) are minimal based on the rare conditions needed to generate the effluents and the small amounts of the effluents that are produced. The carbon dioxide issue is dealt with, with written warnings and labels on the product or instructions informing the user to operate the systems in well ventilated or carbon dioxide monitored spaces. The impact of using the FAFC system in aircraft passenger cabins, with respect to the carbon dioxide emissions and oxygen depletion, should be viewed in terms of the equivalence of the FAFC system to an adult human respiration (as discussed in the risk/safety analysis section).

Testing Protocols and Qualification

The risk/safety analysis section also described in great detail the testing and qualification protocol that will be implemented to ensure appropriate due diligence is done. This section attempts to further clarify some of the unexplained points mentioned in the earlier sections with respect to testing and qualification.

International Electro-technical Commission (IEC) Micro Fuel Cell Safety Standard

The micro fuel cell industry, Underwriter's Laboratory (UL) and Canadian Standards Association (CSA) are working with the IEC (via the TC 105 sub-committee) to develop international safety standards for micro fuel cells. The safety standard is in the final stages of completion and the goal of the safety working group, in-charge of the safety standard, is to have an IEC standard in place by the middle to end of 2006. The safety standard will specify requirements and provide guidelines for evaluating the product to the requirements. The general category of requirements will be in the context of the discussion that was pursued in the risk/safety analysis section of this document.

Third Party Laboratory Testing

The independent third party test laboratory mentioned in the earlier parts of the document is referring to the equivalent of Underwriter's Laboratory (UL) and Canadian Standards Association International (CSA). Such test facilities have been in the independent product testing and certification business for many years and have also acquired valuable testing and safety evaluation experience with fuel cells in the last five to ten years. These testing facilities also have many years of experience in cross referencing other appropriate safety standards for refining or adding requirements when the need arises. The basis of their product testing and certification issuing is qualification of the existence of sufficient safety and non-existence of unacceptable risks for the duration of the products life.

— END —