DANGEROUS GOODS PANEL (DGP)

TWENTIETH MEETING

METHANOL MICRO FUEL CELL

(Presented by H. Okayama)

This information paper contains the following documents:

1. Direct Methanol Fuel Cell (DMFC) Risk Analysis
2. DMFC Type Test
3. Reformed Methanol Fuel Cell (RMFC) Risk Analysis
4. RMFC Type Test
5. Methanol Clathrate Compound (MCC) Risk Anaysis
6. MCC Type Test

ICAO Member Briefing

Passenger and Crew Exception for Direct Methanol Fuel Cells

ICAO DGP twentieth meeting in Montreal

Oct. 24－Nov. 4

Prepared by Japan Electrical Manufacturers' Association (JEMA)

Introduction

With the advent of the ubiquitous information society, there will be a growing demand for high density electric power sources beyond the capabilities of the existing battery systems for portable communications and computing devices such as laptop computers, cell phones and PDAs. Micro fuel cells have attracted great attention as potential candidates to replace batteries in portable applications due to recent technological developments that pave the way to achieve outstanding performance and benefits, including longer runtimes and longer lifecycle performance than even the most advanced battery systems. Among micro fuel cells, Direct Methanol Fuel Cells (DMFCs) offer promising prospects since methanol can be readily handled, and compact and light devices can be realized, thus they have high expectations as power sources for portable devices.

Background

As a result of the technological achievements during the last decade, DMFC commercialization, for limited applications, was realized in 2003. However, the deregulation and safety standard of methanol cartridges, which are indispensable for widespread use of DMFCs, are yet to be defined.

The work on deregulation and safety of DMFCs was initiated at the beginning of 2000's, worldwide. As outcomes of these studies, several presentations were made to the United Nations Sub-Committee of Experts on the Transport of Dangerous Goods (UN SECTDG) to explain the DMFC technologies and basic safety features by the US in 2003 and by the US and Japan collaboratively in 2004. Consequently, the UN approved a new entry designated as UN3473 for fuel cell cartridges containing flammable liquids including methanol, in December 2004.

Moreover, similar presentations were collaboratively made to the ICAO DGP WG by the US and Japan in October 2004 and in April 2005. At the latter meeting, Japan submitted a proposal for exclusion of passengers carrying methanol fuel cells and methanol cartridges on aircraft from the existing aviation regulations. During this meeting, many comments and advice have been received concerning the Japanese proposal and the Dangerous Goods Advisory Council (DGAC) submitted a document suggesting revised wording of the Japanese proposal. However, at that time, International Electrotechnical Commission (IEC) standard for DMFC systems had not been concluded into the final draft, and therefore, ICAO put off the decision to until the October 2005 meeting, when the IEC standard final draft is expected to be ready.

IEC Standard

IEC 62282-6-1 standard for safety of micro fuel cell power systems has been circulated in August 2005 and will be published by the end of 2006. It covers micro fuel cell-powered systems not exceeding 60 volts and 240 watts and fuel cartridges. And the cartridges should be designed so as not to be refilled by the consumer. The standard includes the safety of normal use, reasonably foreseeable misuse, and when carrying methanol fuel. The general design requirements have been decided to avoid risks of fire, explosion, leakage, harmful emissions, and ignition sources. The design should be tolerant to temperature extremes, vibration, high internal pressure, low external pressure, crushing, dropping, and connection & disconnection, so as to prevent leakage. Extensive type testing should be performed on DMFC systems. User instructions and warnings should be provided.

Risk and safety analysis is described in Appendix A, and **a summary of type test items** is shown in Appendix B.

Appendix A. Risk and Safety Analysis

Micro fuel cell power systems, power units, and fuel cell cartridges are subjected to safety testing in accordance with the IEC 62282-6-1 safety standard. The type test requirements for DMFC systems that directly produce electricity by methanol are specified in the main body of the safety standard.

Risk and safety analysis performed on DMFC systems focuses on various product design controls and testing procedures to prevent critical safety failures and to eliminate possible risks. The table given below summarizes the potential risks and risk mitigations that can be proved through physical analysis and/or testing to assure safety during normal use, foreseeable misuse, and transportation through the lifespan of the product. In this table, numbers in parentheses in the “Risk Mitigations” column indicate the corresponding item numbers in the “Risk Description” column.

	Risk Description	Risk Mitigations
1	Methanol or methanol/water solutions leak out of fuel cartridge from exposure to environmental or handling stress through: 1. **Pressure differential (Altitude change)** 2. **Vibration** 3. **Temperature cycling** 4. **High temperature exposure** 5. **Dropping** 6. **Compressive loading** 7. **Cartridge components material degradation failure during lifetime of the product** leading to: - personal injury from ingestion (toxic) - damage to equipment or personal injury from ignition of flammable liquid	* (1,2,3,4,5,6,7) The DMFC fuel cartridge will be provided with sturdy and rigid plastic container with a valve, and designed as a non-refillable type, which means the fuel cartridge is to be replaced with a new one whenever the fuel in the cartridge is depleted. The DMFC fuel cartridge shall comply with the IEC 62282-6-1 safety standard to withstand under normal use, reasonably foreseeable misuse and consumer transportation. * (1) The DMFC cartridge will be designed and verified to withstand in the case of altitude changes in aircraft. <95 kPa differential pressure for 30 min with no fire, no explosion, no leakage, and no fuel vapor loss> * (3,4) The DMFC cartridge will be designed and verified to withstand temperature changes and high temperature exposure. <+55ºC 4 hrs/-40ºC 4 hrs 2 cycles with no fire, no explosion, no leakage, and no fuel vapor loss > <+70ºC for 4 hrs with no fire, no explosion, no leakage, and no fuel vapor loss > * (2) The DMFC cartridge will be designed and verified to withstand normal transportation vibration. <7 Hz - 200 Hz/15 min sweep total 3 hrs with no fire, no explosion, no leakage, and no fuel vapor loss > * (5) The DMFC cartridge will be designed and verified to withstand inadvertent drop. <1.8 m to the hard wood with no fire, no explosion, no leakage, and no fuel vapor loss > * (6) The DMFC cartridge will be designed and

		verified to withstand the forces reasonably encountered due to being stepped on or something heavy being placed on the fuel cartridge. <100 kg/5 sec with no fire, no explosion, no leakage, and no fuel vapor loss > * (7) The DMFC cartridge components /materials which are in direct contact with methanol will be checked for durability over the product life. * (1,2,3,4,5,6,7) Marking will be placed on the fuel cartridge for caution. <e.g. DO NOT DISASSEMBLE, AVOID CONTACT WITH CONTENTS etc.>
2	Methanol or methanol/water solutions leak out of DMFC unit or system (cartridge and fuel cell power unit) from exposure to environmental or handling stress through: **1. Pressure differential (Altitude change)** **2. Vibration** **3. Temperature cycling** **4. Dropping** **5. Compressive lording** leading to: - personal injury from ingestion (toxic) - damage to equipment or personal injury from ignition of flammable liquid	* (1,2,3,4,5) The DMFC system complies with the IEC 62282-6-1 safety standard to withstand under normal use, reasonably foreseeable misuse and transportation. * (1) The DMFC system will be designed and verified to withstand in the case of altitude changes of aircraft. <95 kPa differential pressure for 30 min with no fire, no explosion, no leakage, and no fuel vapor loss > * (3,4) The DMFC system will be designed and verified to withstand temperature changes <+55ºC 4hrs/-40ºC 4hrs 2 cycles with no fire, no explosion, no leakage, and no fuel vapor loss > * (2) The DMFC system will be designed and verified to withstand normal transportation vibration. <7 Hz - 200 Hz/15 min sweep total 3 hrs with no fire, no explosion, no leakage, and no fuel vapor loss > * (4) The DMFC system will be designed and verified to withstand inadvertent drop. <1.2 m to the hard wood with no fire, no explosion, no leakage, and no fuel vapor loss > * (5) The DMFC cartridge will be designed and verified to withstand the forces reasonably encountered due to being stepped on or something heavy being placed on the fuel cartridge. <25 kg/5 sec with no fire, no explosion, no leakage, and no fuel vapor loss >
3	Leakage from the fuel cartridge valve leading to: - personal injury from ingestion (toxic)	* The DMFC fuel cartridge valve is always closed while the fuel cartridge is detached from the DMFC, and designed not to be able to open the valve manually. The valve only allows the fuel feed when the fuel cartridge is properly

	- damage to equipment or personal injury from ignition of flammable liquid	attached to the fuel cell. * The valves shall not be susceptible to unintended actuation, or manual actuation by the user not using tools, which results in fuel leakage. Compliance shall be checked using test probe 11 of IEC 61032.
4	Leakage during the fuel cartridge connecting and disconnecting (considering connection cycling)	* The valve of DMFC fuel cartridge withstands up to 10 cycles and the valve of DMFC system withstands up to 1000 cycles. <no fire, no explosion, and no leakage >
5	Allowable surface temperature of the DMFC system	* The DMFC system will be designed in order not to exceed the its surface temperature, depending on the material, as follows: Metals: 50ºC Molded resin/rubber/wood: 70ºC * The thermal protection circuits (e.g., temperature detectors like thermistors, temperature fuses) will be actuated to prevent from abnormal temperatures. This measure will be adopted by each manufacturer. * During normal operation, methanol is consumed only for the electrochemical reaction, not for burning.
6	Concerning charging of rechargeable batteries	* The battery charge circuit shall stop the charging when the rechargeable batteries are fully charged. Also, the protection circuits will be equipped with second layer protections; this will cut off the current if the first protection layer is broken.
7	Wrong fuel cartridge (Formic acid etc.) applies to DMFC system	* Each fuel cartridge shall have a key to prevent wrong fuel cartridge connections according to the IEC TC 105 interchangeability standard.
8	DMFC system (cartridge and fuel cell power unit) may be damaged under reasonable consumer use and abuse situations so that the fuel may leak out or may be accessed. leading to: - personal injury from ingestion (toxic) - damage to equipment or personal injury from ignition of flammable liquid	* The DMFC system shall comply with the IEC Micro Fuel Cell Standard, which is a consumer based safety standard that covers all the anticipated use and abuse conditions. The standard has been formulated referring to many other consumer product safety standards. * Many type tests (e.g., temperature cycling, high temperature exposure, pressure difference, vibration, drop, compressive loading, external short-circuit, surface and exhaust gas temperature, long-term storage, high temperature connection, connection cycling) will be performed to simulate various effects of

		predictable hazards in situations where consumers normally use micro fuel cells, in order to ensure the safety of fuel cartridges, micro fuel cell power units or micro fuel cell power systems. * Cartridge and fuel cell system will be designed to ensure no leakage occurs as a measure of risk mitigations mentioned in item 1. * The DMFC system will be designed tamper proof, so that without special tools (e.g., screw driver, metal knife, hammer) the system may not be taken apart and the fuel may not be accessed. * Labels will be placed on the cartridge and fuel cell system with accompanying literature, warnings against flammability, toxicity, exposure to children, exposure to heat or flame.
9	Methanol or methanol/water solutions ignition and fire catching leading to: - causing personal and property damage	* Tests by Japan showed that methanol or methanol/water solutions do not explosively ignite. Auto ignition temperature of pure methanol is 470ºC. Flash points of methanol or methanol and water solutions are nearly identical to those of ethanol (e.g., alcohol beverages) * All electronics in the fuel cell system will be non-arcing and non-sparking. * A short circuit test will be conducted in which the fuel cell system is short circuited for 5 min. During or after this period, the system would not catch fire, explode and leak, and also the exterior surface temperature would not reach to an unacceptable level. * Labels will be placed on the cartridge and fuel cell system with accompanying literature, warnings against flammability, exposure to heat or flame.
10	Emissions of CO/CO_2 gas and organic compounds such as methanol, formaldehyde, formic acid and methyl formate may cause under storing or operating conditions of micro fuel power unit or micro fuel cell power system, which is fuelled with methanol. leading to: - personal injury from inhalation (toxic)	* The maximum emission rate for each of the constituents of interest shall be less than the emission rate limit value as follows: Methanol 2600 mg/hr Formaldehyde 0.6 mg/hr CO 290 mg/hr CO_2 60000 mg/hr Formic acid 90 mg/hr Methyl formate 2450 mg/hr Water No limit

		* The emission rate limit was decided based on 10 $m^3 \cdot$ ACH, obtained as the product of the reference volume and the number of times of air changes per hour (ACH), because it covers the reasonably foreseeable environments where DMFC system is expected to be used. * The interior space in a small car and the minimum volume per person on commercial aircraft is 1 m^3. The minimum ACH used on passenger aircraft is 10 and the lowest ventilation setting in a car is 10 ACH. Buildings may have ACH levels as low as 0.5, but the volume per person is over 20 m^3, so that the product remained unchanged at 10. * Note: A seated adult has a CO_2 emission rate of 30000 mg/h (15.3 L/hr). The fuel cell plus human emission rates are limited to 9 g/m^3. This suggests that the allowable fuel cell emission rate should be below 60000 mg/h (30.5 L/hr). If 200 ml of methanol is fully consumed in cabin during 10 hours, the quantity of CO_2 emission during operation is 11.8 L/hr. This figure is found to be lower than that of CO_2 generated during respiration of a seated human adult.
11	Operation of the DMFC system may cause oxygen depletion to below 18% levels (considered unsafe threshold for humans) and challenges the comfort levels in passenger cabins of aircraft. Leading to: - Personal injury due to oxygen depletion	* The fuel cell system will be designed taking into account the appropriate oxygen consumption control strategy so that the fuel cell system can be operated in conjunction with a person in a 1 m^3 air volume with10 ACH without depleting oxygen levels below 18 %. * 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 devices should be used in adequately ventilated areas. * Note: If 200 ml of methanol is fully consumed in cabin during 10 hours, the quantity of O_2 consumption during operation is 16.8 L/hr. This figure is found to be lower than that of O_2 consumption (26.4 L/hr) during respiration of a seated human adult.
12	Product flammability hazard – materials coupled with fuel vapor, ignition sources, and electrical heat may cause fire.	* Materials of components which are in direct contact with methanol or methanol/water solutions shall be flame-resistant. * Potential ignition source(s) will be eliminated within areas where fuel is placed. * A fire enclosure is required when temperatures of the parts under fault conditions are sufficient for ignition.

		* Auto ignition temperature of pure methanol is 470 ºC. * IEC Micro Fuel Cell Safety Standard checks for flammability classes of the materials of components and other parts located outside fire enclosures. * All electronics in the fuel cell power system will be non-arcing and non-sparking. * Control system monitor current will draw and trigger system shut down in an over-current situation. * Equipment will be designed to limit the risk of fire due to mechanical or electrical overload or failure, or due to abnormal operation or careless use. * A short circuit test will be conducted where the fuel cell system is short circuited for 5 minutes. During or after this period, the system would not catch fire, explode, leak or reach an unacceptable surface temperature for the housing materials. * Labels will be placed on the product or included with accompanying literature, warnings against exposing the fuel cartridge to heat or flame above 50 ºC.
13	Long term storage of fuel cartridges at elevated temperature (50 ºC) can lead to fuel leakage leading to: - personal injury from exposure to fuel vapor (toxic)	* Micro Fuel Cell Safety Standard requires long-term storage testing of fuel cartridges to simulate the effects of long term storage at elevated temperature (50 ºC, 28 days) to ensure no leakage. * Labels will be placed on the product or included with accompanying literature, warnings against storage at elevated temperatures.

Note 1:

1) UN 3473 “FUEL CELL CARTRIDGES containing flammable liquids” has been listed.
2) ICAO Dangerous Goods Carried by Passengers or Crew.
   TI 8-1-1-2b) non-radioactive medicinal or toilet articles: The total net quantity of all such articles carried by each person must not exceed 2 kg or 2 L and the net quantity of each single article must not exceed 0.5 kg or 0.5 L. The term “medical or toilet articles” is intended to include such items as hair sprays, perfumes, colognes and medicines containing alcohols”.

Note 2: Methanol toxicity

UN ENVIRONMENT PROGRAMME INTERNATIONAL LABOUR ORGANISATION WORLD HEALTH ORGANIZATION INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY

ENVIRONMENTAL HEALTH CRITERIA - 196 Methanol

*Acute inhalation of methanol vapor concentrations below 260 mg/m^3 or ingestion of methanol liquid up to 20 mg/kg by a healthy or moderately folate-deficient human should not result in formate accumulation above the endogenous levels.

*A widely used occupational exposure limit for methanol is 260 mg/m^3 (200 ppm), which is determined to protect workers from any of the effects of methanol induced formic acid metabolic acidosis and ocular and nervous system toxicity.

*No other adverse effects of methanol have been reported in humans except minor skin and eye irritation at exposures well above 260 mg/m^3 (200 ppm).

*For a reference 10 kg child (US CPSC reference child is 11.35 kg), 20 mg/kg be equivalent to 200 mg or 0.25 ml. This is about 5 drops of 100% methanol.

Appendix B

DMFCs (Direct Methanol Fuel Cells) Leakage definition and Type test items of Committee Draft by IEC/TC105 Micro Fuel Cell Safety WG8

Leakage Definitions

1.NO LEAKAGE	No accessible hazardous liquid fuel outside the system or cartridge.
2.NO FUEL VAPOR LOSS	Fuel vapor escaping from the cartridge or system is less than 0.33 g/hr.
3.HAZARDOUS LIQUID FUEL	Any liquid fuel amount over 5 ml or a concentration of methanol greater than or equal to 4% by weight in water.
4.NO ACCESSIBLE LIQUID	Consumer cannot come into physical contact with HAZARDOUS liquid fuel.

Type Tests

Purpose : The type tests for micro fuel cell systems, fuel cell power units and fuel cartridges provide that these systems are safe for normal use , reasonably foreseeable misuse, and consumer transportation.

Requirements : Most of type tests require "No leakage, no fuel vaporloss, no fire and no explosion"

Test Item	Purpose	Test sample	Test Conditions and Test Procedures	Requirements
1.Pressure differential tests*	To simulate the effects of a high internal pressure or low external pressure and ensure no leakage.	unused Fuel cartridge	1) An internal Pressurization or 2) Low External Pressure test shall be done. 1) >**95 kPa gage pressure plus normal working pressure at RT*** or 2 times the vapor pressure of the fuel at 55ºC for 30 minutes** at room temperature. 2) **95 kPa differential applied for 30 minutes. (for a rigid cartridge)**	1) Internal Pressurization No accessible liquid test medium leakage and no sudden drop of pressure. 2) Low External Pressure No fire at any time, no explosion at any time, no leakage, no fuel vapor loss.
		Micro fuel cell power unit or power system	Both 1) Test A and 2)Test B shall be done. 1) Test A : **68 kPa for 6 hours** at RT. 2) Test B : **95 kPa differential pressure for 30 minutes** at RT.	1) Test A No fire at any time, no explosion at any time, no leakage, no fuel vapor loss. 2) Test B fuel vapor loss less than 20g/hr
2.Vibration test*	To simulate the effects of normal transportation vibration and ensure no leakage.	unused Fuel cartridge and Micro fuel cell power unit or power system	**7 Hz (peak acceleration of 1 gn) and 200 Hz (peak acceleration of 8 gn) and back to 7 Hz traversed in 15 minutes.** This cycle shall be repeated 12 times for a total of 3 hours for each of three mutually perpendicular	No fire at any time, no explosion at any time, no leakage, no fuel vapor loss.
3.Temperature cycling test*	To simulate the effects of low temperature and high temperature exposure and the effects of extreme temperature change .	unused Fuel cartridge and Micro fuel cell power unit or power system	**-40ºC 4 hours to 55ºC 4 hours 2 times**	same as above
4.High temperature exposure test	To simulate the effects of a fuel cartridge left in high temperature environments.	unused Fuel cartridge	**70±2ºC for 4 hours**	same as above
5.Drop test	To simulate the effects of an inadvertent drop and ensure no leakage.	unused Fuel cartridge and Micro fuel cell power unit or power system	The test sample shall be dropped on the horizontal surface consists of hardwood 1.from **120 cm** in hight for a fuel cell power unit or system 2.from **180 cm** in hight for a fuel cell cartridge The drop shall be carried out towards 4 directions(valve up, valve down and two other mutually perpendicular dorections.	same as above
6.Compressive loading test	To simulate the effects of the forces reasonably encountered due to being stepped on or something heavy being placed on the fuel cells	unused Fuel cartridge and Micro fuel cell power unit or power system	1. **25 kg for 5 sec**. : A fuel cell power unit or system 2. **100 kg for 5 sec**. : A fuel cell cartridge	same as above
7.External short-circuit test	To simulate the effects of an external short circuit.	Micro fuel cell power unit or power system	**0.1 ohm for at least 5 minutes**.	same as above
8.Surface and exhaust gas temperature test	To eliminate any risk of burn injury caused by contact with the enclosure of fuel cell power system or blown exhaust gas from the vent.	Micro fuel cell power unit or power system	1.To measure the temperature of the bare surface of micro fuel cell power units and/or micro fuel cell power systems operating at rated output. 2.To measure the temperature of exhaust gas within 1 cm of the exhaust vent of micro fuel cell power units and/or micro fuel cell power systems operating at rated output.	no burn (The maximum temperature at the casing surface shall not exceed the specified values depending upon the material which are shown in Table4.18.1 of IEC-62282-6-1safety standard. The temperature at 1 cm of the exhaust vent of operating micro fuel cell shall be less than 70ºC.)
9.Long-term storage test	To simulate the effects of long term storage at elevated temperature upon a fuel cell cartridge and ensure no leakage .	unused Fuel cartridge	**50ºC for 28 days**	No fire at any time, no explosion at any time, no leakage, no fuel vapor loss.
10.High temperature connection test	To simulate the effects of mating and un-mating of the fuel cartridge to the fuel cell power unit at an elevated temperature and ensure no leakage, no fire, no explosion.	unused Fuel cartridge and Micro fuel cell power unit	The test cartridge is kept in the chambercontrolled at temperature of **50±2ºC for 4 hours**. And the test FC power unit is kept at RT.	No fire at any time, no explosion at any time, no leakage.
11.Fuel cell power unit internal pressure test	A) To test those parts of the fuel cell power system that maintain a high fuel pressure during operation or storage such as the sections between the cartridge and the system including the regulator valve or fuel pump or whatever is subject to a high pressure. B) To test that there is no leakage at the cartridge connection.	Micro fuel cell power unit or power system using pressurized cartridge	**>95 kPa plus normal working pressure or two times fuel vapor pressure at 55ºC for 30 minutes.**	No accessible liquid test medium leakage. No sudden drop in pressure.
12.Connection cycling test****	To simulate the effects of mating and un-mating of the fuel cartridge to the fuel cell power unit and ensure no leakage.	unused Fuel cartridge and Micro fuel cell power unit or power system	Fuel cartridges shall be repeatedly mounted on and dismounted from micro fuel cell power unit specified repetition cycles. 1.For a fuel cell power unit:thousand **(1000) cycles** desorption. 2.For a fuel cartridge except satellite cartridge: a minimum of **ten (10) cycles** desorption. 3.For a satellite fuel cartridge: a minimum of fifty **(50) cycle** desorption.	No fire at any time, no explosion at any time, no leakage.
13.Emission Test**	To ensure safe emissions levels of all possible emissions, under storage or operating conditions.	Micro fuel cell power unit or power system	To measure the concentration of emission gas from a fuel cell power system operating at rated power	For a 1 m^3 chamber at 10 air change per hour (ACH).Emissions limits are as follows: Methanol: 2600 mg/hr, CO: 290 mg/hr, CO_2: 60000 mg/hr, Formaldehyde: 0.6 mg/hr, Formic Acid: 90 mg/hr, Methyl formate: 2450 mg/hr

* Sequential Test	For a fuel cartridge, Vibration test and Temperature cycling test shall be done sequentially (Vibration test -> Temperature cycling test)
	For micro fuel cell power unit or power system, Pressure differential test, Vibration test and Temperature cycling test shall be done sequentially (Pressure diffrential test -> Vibration test -> Temperature cycling test).
** Emission Test	Emission test shall be done after each type test for a micro fuel cell power unit or power system is carried out.
*** RT	Room temperature 22±5ºC
**** Connection cycling test	As for a detail process, refer to 7.3.12 of IEC-62282-6-1safety standard.

Risk Assessment of Micro Reformed Methanol Fuel Cells:

Safe and Advanced Portable Power for Today's Portable Device Demands

Whitepaper prepared by the International
Electrotechnical Commission (IEC) Task Group for
Reformed Methanol Fuel Cell Safety

Prepared for International Transportation
Regulators and Advisors

July 2005

Table of Contents

Introduction

Methanol fuel cells offer the promise for portable power of smaller packages, longer runtimes, and the elimination of the need to recharge batteries. These systems will soon power a range of portable devices, such as laptop computers, cell phones, or PDAs, and users will want to carry these ubiquitous devices onboard commercial aircraft. Before this can happen, methanol fuel cell manufacturers must demonstrate the inherent safety of their products, and proper standards and regulations need to be set in place.

This whitepaper will address this topic for micro reformed methanol fuel cell (RMFCs), which will begin commercialization in 2006. RMFCs differ from their counterparts, direct methanol fuel cells (DMFCs), in that an RMFC will "reform" methanol fuel into hydrogen and carbon dioxide immediately before being consumed by the fuel cell.[*] DMFCs consume the methanol "directly," without such conversion taking place. RMFCs offer the advantage of high performance PEM fuel cells, while leveraging the simplicity and convenience of methanol fuel. From a safety and regulatory standpoint, RMFCs and DMFCs are largely the same, given that they use the same types of cartridges and fuel and employ many of the same tests. Both RMFCs and DMFCs will be subject to rigorous design type tests to demonstrate their high integrity, including the prevention of methanol leaking out due to adverse conditions that might occur during the course of their use.

This whitepaper explains how fuel cells and, specifically, RMFCs work and provides a detailed risk assessment of RMFCs. Section 1 of this document provides a basic overview of fuel cells and RMFCs. Sections 2 and 3 address specific key functions in an RMFC – outlining RMFC thermal and emissions management, respectively. Section 4 is a detailed risk assessment, covering all aspects of the RMFC, including emissions, temperatures, catalysts, and the fuel cartridge. Finally, Section 5 provides a brief summary of the international product safety standard (IEC 62282-6-1) that will be used in safety certification of RMFCs and other micro fuel cell types.

It is the recommendation of the RMFC safety task group that RMFCs and DMFCs are considered jointly as *Methanol Fuel Cells* before the ICAO Dangerous Goods Panel in October 2005 and that RMFCs are approved for use by passengers onboard commercial aircraft.

[*] Note that "RMFCs" and "DMFCs" refer to micro RMFCs and micro DMFCs in this document. Both of these subtypes are covered by the IEC safety standard 62282-6-1. There are other size classes of these types of fuel cells, but these classes are not discussed in this whitepaper.

Section 1. Basics of fuel cells and RMFCs

This section provides a basic overview of the operation of RMFCs and fuel cells.

How do RMFCs work?

Figure1 shows the basic components and processes of an RMFC: On an as-needed basis, methanol-water fuel is fed to the reformer. The reformer then converts or "reforms" the methanol to reformate, which consists of hydrogen and carbon dioxide, and this reformate is immediately consumed by the fuel cell stack. By intaking ambient air, the system produces electricity, while giving off water vapor, carbon dioxide, and unconsumed air. Additionally, the incoming air provides cooling for the system. Trace levels of other emissions are possible, but will be at low and safe levels. See Section 4 of this whitepaper for a detailed discussion of this.

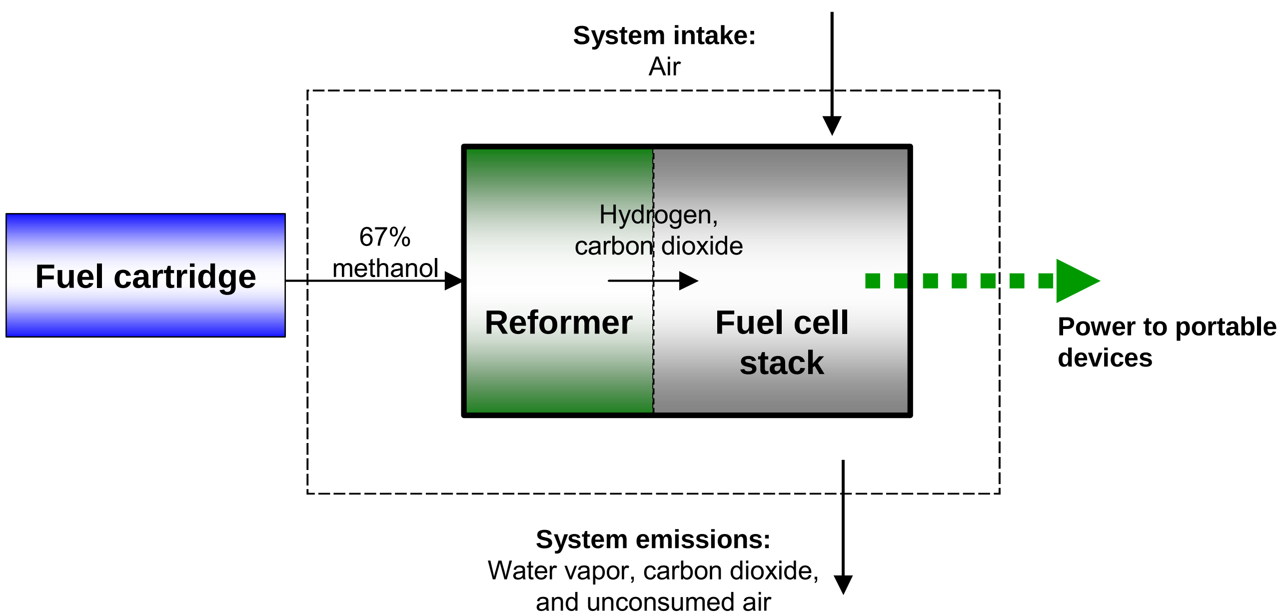

Figure1. Basic schematic of a micro RMFC*

What is the fuel cell stack?

A fuel cell is like a battery in that it relies on chemical reactions to silently release energy in the form of electricity. However, it is also fundamentally different than a battery in how it is 'refueled': fuel cells do not need to be thrown away or undergo time-consuming

* Note that the fuel in this example is 67% methanol and 33% water (by volume). In some cases, the methanol concentration is as high as 100%.

recharging. Instead, they provide electricity as long as fuel is available. At the heart of any fuel cell system is the fuel cell stack, which produces the system's electricity.

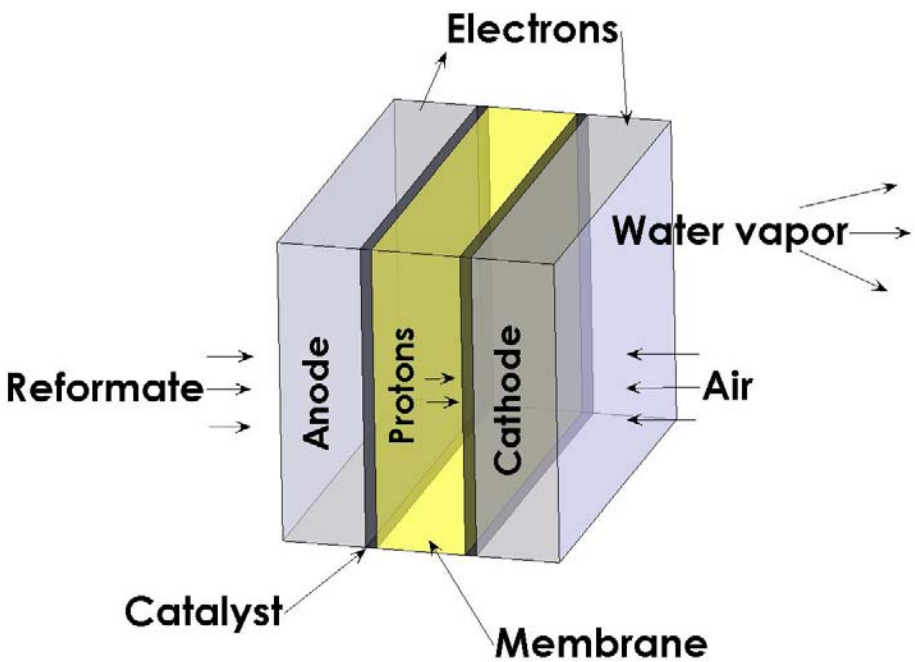

Figure 1. Diagram of a single cell

Figure 2 provides the basics of a "single cell" within a fuel cell system. In this type of fuel cell, reformate (hydrogen and carbon dioxide) is fed to one side of the fuel cell and air is fed to the opposite side. Under an electrical load, like a laptop computer, hydrogen in the reformate and oxygen in the air react to create electricity, heat, and water. These single cells are then "stacked" together as the fuel cell stack to achieve the desired operating voltage and power capabilities.

Section 2. Moderate temperature operation of micro RMFCs

This section details how micro RMFC manufacturers approach thermal management and provide an inherently safe system from the standpoint of temperature. The user of a micro RMFC experiences surface and exhaust temperatures comparable to laptop computers and other low temperature micro fuel cells. During operation, localized temperatures within the reformer and fuel cell stack are higher. However, similar to the high temperatures seen in a laptop computer processor chip, insulation and air cooling provide straightforward means of containing localized higher temperatures.

How is the end user isolated from localized high temperatures?

Figure 2 shows the liquid and gas flows in and out of a micro RMFC system. Methanol fuel and oxygen from ambient air are fed to the system, and carbon dioxide, water vapor, and unconsumed air are exhausted.

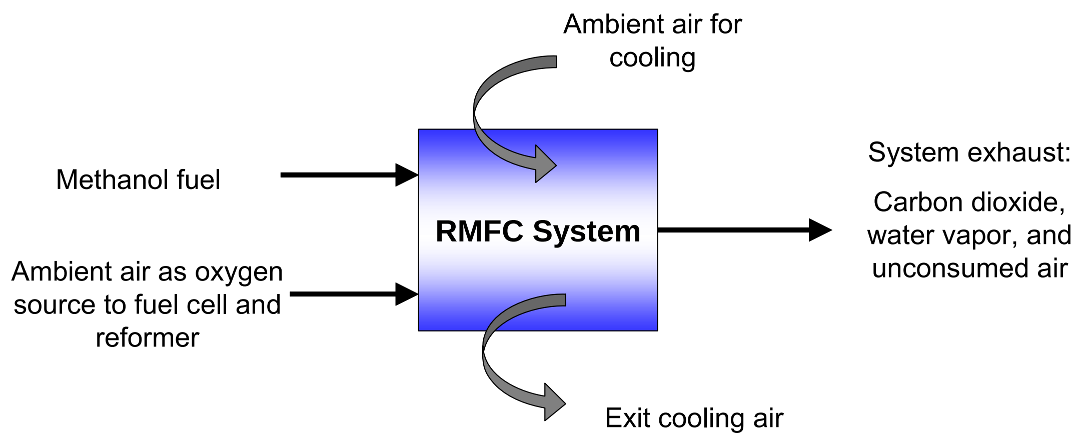

Figure 2. Liquid and gas flows in an RMFC

A detailed breakdown of the thermal management is shown in Figure 3. This schematic shows that the reformer operates at approximately 280°C, and the fuel cell stack will operate in the range of 80-180°C, depending upon the stack technology of choice. RMFC reformer temperatures do not exceed 300°C. These localized higher temperatures are contained by layers of insulation (typically less than 0.5 in.) with the external surface of the insulation at temperatures in the range of 60-90°C. These temperatures are then dropped through air cooling to 30-60°C, which is the outer case temperature that the end user sees. The temperature of gases leaving the reformer at 280°C is quickly dropped to 40-70°C by mixing these hot gases with cooling air.

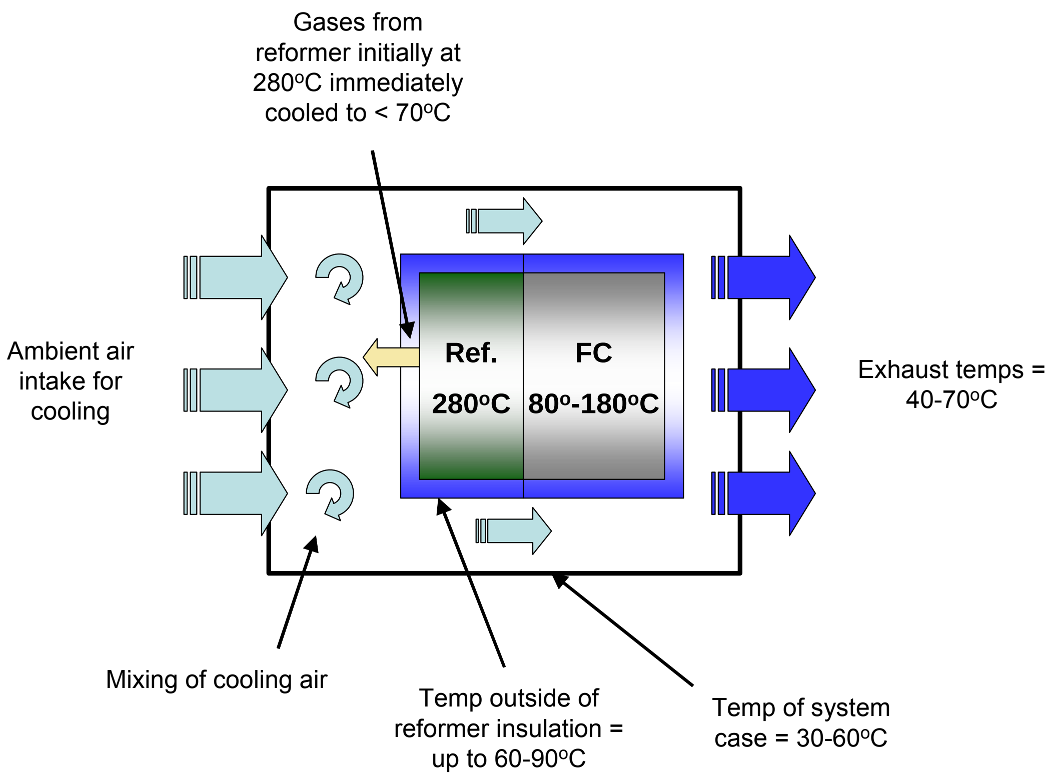

Figure 3. Thermal management in a micro RMFC

This simple and robust thermal management system shows how local higher temperatures are dropped readily with insulation layers. A variety of insulators are well known that can provide these temperature drops.[1] Isolating these local high temperatures is therefore a straightforward task with available insulators. The main thermal management challenge is thus removing the inherent heat generated in any micro fuel cell. The following evaluation shows how micro RMFCs fundamentally and safely address this.

How much heat do RMFCs give off?

Ultimately, the challenge of thermal management is dominated by the amount of heat produced by the system.* Figure 4 shows how much heat would be generated by a typical RMFC used to power laptop computers.** This graphic shows that the amount of heat produced for a given application is only dependent upon the net efficiency: the higher the efficiency, the lower the amount of waste heat generated. In this scenario, 47 W of heat must be removed to prevent overheating. For a laptop micro fuel cell that runs at an

* *Temperature* is defined as the degree of hotness or coldness of a body or environment, whereas *heat* is defined as a form of energy that is transferred by a difference in temperature.
** Note that micro fuel cells can have a range of efficiencies. 30% net efficiency is representative of many laptop RMFCs and is a best case scenario for laptop DMFCs. Across all micro fuel cell applications, DMFCs can realistically have efficiencies of 15-30%, and RMFCs can have efficiencies of 20-35%. (Source: Motorola, Casio, UltraCell)

efficiency below 30%, more than 47 W would need to be removed, and the thermal management task would become a more difficult one.

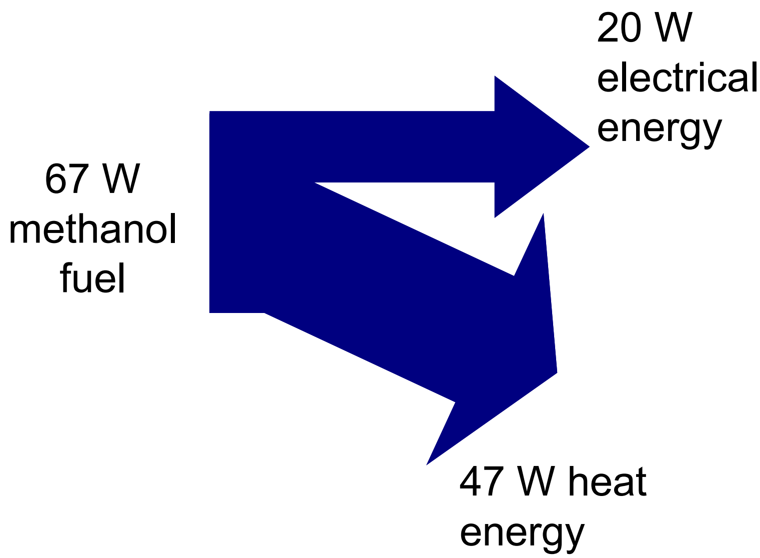

Figure 4. Energy flows for a 20 W RMFC and DMFC systems running at equivalent net efficiencies

What safety redundancies are used to ensure moderate temperatures?

Any consumer device that produces heat can overheat given the necessary abuse. Thus, micro fuel cells incorporate the redundant safety features to ensure overheating does not occur. Equipped with multiple temperature sensors, the micro RMFC system will shut off immediately at above normal temperatures, similar to appliances such as coffee makers. The risk assessment in Section 4 provides further detail on this.

Thermal management summary

Micro RMFCs thus provide high levels of thermal safety. Insulation of localized high internal temperatures safely reduces the temperatures experienced by the user. High efficiencies minimize the challenges of heat management. Finally, proven redundant thermal safety mechanisms protect against any abnormally high temperatures from system abuse.

Section 3. Emissions safety

This section addresses the question of emissions from an RMFC. Unwanted emissions have the potential to exist in all methanol fuel cells. RMFC manufacturers resolve this through the use of a catalytic heater, which safely and fully converts unwanted emissions – including hydrogen and methanol – to carbon dioxide and water.

What is the catalytic heater and how does it ensure safe emissions?

Figure 5 details the gas and liquid flows in the various parts of an RMFC. The entire reformer unit (sometimes called the "fuel processor") is subdivided into two sections. The "reformer" coverts or reforms the methanol to hydrogen reformate. The "catalytic heater" is the other chamber designed to ensure safe emissions and help keep the system warm, especially during system start-up.

The catalytic heater is an inherently robust solution to any unwanted emissions. All system gases pass through it before exiting the system, and it efficiently converts any potential intermediates to carbon dioxide and water. These potential intermediate include methanol, hydrogen, and carbon monoxide, as well as possible trace amounts of formic acid and formaldehyde.[2] The RMFC design, thus, removes unwanted emissions through its catalytic heater by converting these emissions to harmless water vapor and carbon dioxide.*

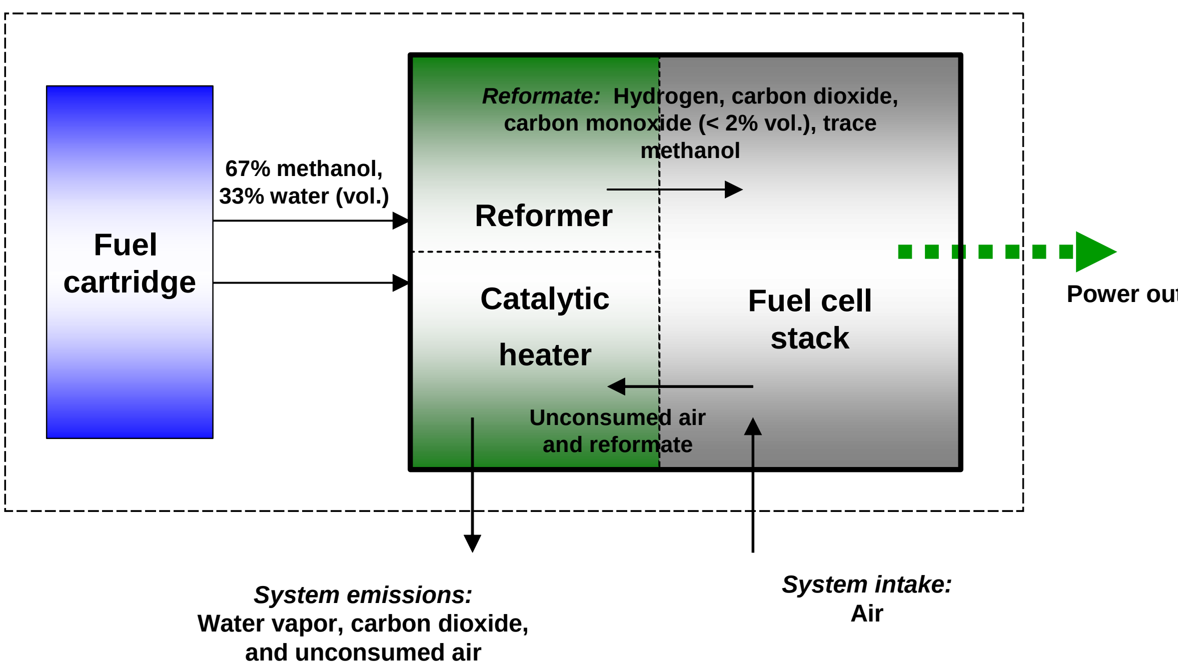

Figure 5. Detail of gas and liquid flows in RMFCs

* Two RMFC systems for laptop computers (20-25 Watt each) will produce carbon dioxide levels approximately equivalent to the level exhaled by an adult human.

Are there hydrogen emissions?

The hydrogen within the system is produced "on demand" and is consumed immediately by the fuel cell stack and the catalytic heater. Thus, the hydrogen is fully consumed inside the system.

The IEC safety standard 62282-6-1 requires that the hydrogen emission rate is maintained at a very low level – less than 3 cc/min from a single source. This level was chosen because, under all circumstances, it is impossible for emitted gas to support a flame. Additionally, IEC testing requires that emissions concentrations never exceed 25% of the lower flammability limit (LFL).

Further, the amount of hydrogen in the system is very low, being equivalent to the energy in less than 1/10 of one drop of alcohol (assuming a drop weighs 0.025 g). It is therefore not a product of the system, but rather a process intermediate that is immediately consumed within the system. Fuel pumping capabilities also ensure that there is a low ceiling on how much hydrogen can be made: a pump going at its maximum rate still leads very low hydrogen production rates. Finally, if there is a small leak, the system will immediately detect this and automatically shutdown.

Emissions safety summary

Safe emissions from RMFCs are therefore addressed through the catalytic heater, low amounts of hydrogen within the system, automatic shutdown, and low ceilings on maximum hydrogen generation rates. This high efficiency component ensures that all gas streams are converted to carbon dioxide and water vapor before exiting the system. Section 4 provides further details on emissions safety.

Section 4. Risk assessment of RMFCs

Risk to address	Risk mitigation
1. How are risks of system overheating addressed?	1. The system is designed and tested to monitor temperature through redundant temperature sensors, and the system will shut down if there is any instance of overheating. This is done through the use of the system's microcontroller, which controls the system functions and will shutoff fuel and air delivery upon sensing an unacceptable high temperature. Temperatures will decrease with fuel and air shutoff. 2. The microcontroller will also physically disconnect the fuel cartridge from system if there is system overheating. 3. Microcontroller failure automatically causes the fuel to shutoff. 4. High temperature zones are reliably insulated and isolated from the rest of the system and user. The fuel cartridge is a separate unit. Temperatures on the outside of the insulation surrounding the reformer unit and the catalytic heater are kept at 60-90^{o}C during normal operation. 5. Excess cooling air flow capacity provides cooling to maintain a safe operating temperature. Product enclosure temperatures are less than 60^{o}C, and system exhaust temperatures are less than 70^{o}C. 6. The system is designed and tested to operate safely at 30^{o}C above the normal maximum operating temperature through high temperature materials and construction. At this elevated temperature, the user will not experience high temperatures (product enclosure temperature will remain less than 60^{o}C, exhaust temperature will remain less than 70^{o}C). 7. High efficiency operation of RMFCs reduces the amount of heat that must be removed from the system. Net efficiencies are typically around 30%.
2. How are risks of user exposure to high temperature mitigated?	The analysis above applies here as well.

3. The catalytic heater is an important component in removing hydrogen and other flammable gas emissions. What is done to mitigate the risk of its failure?	1. The catalytic heater contains no moving parts, thereby making failure unlikely. 2. If a failure were to occur, the loss in catalytic heating capability will cause immediate cooling and system shutdown. Temperatures are continuously monitored through redundant temperature sensors, and the system will shutdown under these conditions. The system's microcontroller controls the system functions and will shutoff fuel and air delivery. 3. The microcontroller will also physically disconnect the fuel cartridge from system if there is abnormal system cooling from catalytic heater failure. 4. Microcontroller failure automatically causes the fuel to shutoff. 5. System cooling will cause significant loss in hydrogen production abilities.
4. What is done to address the risk of a hydrogen reformate leak?	1. If a leak were to occur, the catalytic heater would see abnormally low amounts of hydrogen. This would cause immediate cooling and safe system shutdown. Temperature is continuously monitored through redundant temperature sensors, and the system will shutdown under these conditions. The system's microcontroller controls the system functions and will shutoff fuel and air delivery. 2. The microcontroller will also physically disconnect the fuel cartridge from system if there is system cooling from a leak failure. 3. Microcontroller failure automatically causes the fuel to shutoff. 4. System cooling such as this will cause significant loss in hydrogen production abilities. 5. The loss in hydrogen reformate would cause an immediate drop in fuel cell stack voltage, thereby initiating safe system shutdown.
5. If fuel delivery to the reformer is too high, excess hydrogen will be generated. Possible reasons for such failure include poor calibration and a valve failing to close. What is done to mitigate this risk?	1. If too much hydrogen reformate is fed to the system, the catalytic heater will consume this reformate, the system will immediately heat up and will safely shut down. Temperature is continuously monitored through redundant temperature sensors and shuts down with any overheating. The system's microcontroller controls the system functions and will shutoff fuel and air delivery. 2. The microcontroller will also physically disconnect the fuel cartridge from system if there is system overheating such as this. 3. Microcontroller failure automatically causes the fuel to shutoff.

6. How is the entire system constructed to prevent unsafe hydrogen emissions?	1. The catalytic heater eliminates hydrogen before the product stream exits the system. 2. The total amount of hydrogen in the system at any one time contains very low energy content (equivalent to less than 1/10 of one drop of methanol, assuming a drop weighs 0.025 g). 3. Systems are designed and tested to emit hydrogen at safe levels. These limits for these emissions are: - Hydrogen emissions are less than 3 cc/min from a point source. At this level, it is impossible to support a flame. - Hydrogen concentration in a 1 m^3 chamber at 10 air changes per hour (ACH) is less than 25% LFL (1% hydrogen). (Source: IEC 62282-6-1) 4. The system is designed to detect hydrogen leaks (through temperature and voltage sensors as outlined in Items 3-5) and automatically shuts down when a leak occurs. The system's microcontroller controls the system functions and will shutoff fuel and air delivery when unacceptable readings are detected. 5. The microcontroller will also physically disconnect the fuel cartridge from system if there is system cooling from a leak failure. 6. Microcontroller failure automatically causes the fuel to shutoff.
7. How are risks of other potentially harmful emissions mitigated? (e.g., methanol, carbon monoxide, hydrogen, formaldehyde, formic acid).	1. Catalytic heater(s) eliminates harmful gases before exiting the system through oxidation of these gases to carbon dioxide and water vapor. 2. The fuel cell stack also helps to eliminate harmful gases before exiting the system through oxidation of these gases to carbon dioxide and water vapor. 3. The system designed and tested to have safe emissions. The limits for potential emissions are: Water — No limit Methanol — 2600 mg/hr Formaldehyde — 0.6 mg/hr Carbon monoxide — 290 mg/hr Carbon dioxide — 60,000 mg/hr Formic acid — 90 mg/hr Methyl formate — 2450 mg/hr The emission rates are based on maintaining safe concentrations in a 1 m^3 chamber with 10 air changes per hour (ACH). This gives a product of 10 ACH • m^3. This product was selected because it covers the reasonably foreseeable environments where micro fuel cell systems will be used.

	The interior space in a small car and the minimum volume per person on commercial aircraft is at 1 m^3. The minimum ACH used on passenger aircraft is 10 ACH, and the lowest ventilation setting in cars is 10 ACH. Homes and offices may have ACH levels as low as 0.5, but the per person volume is over 20 m^3, so a product of 10 ACH• m^3 is conservative. Note that a seated adult has a carbon dioxide emission rate of 30,000 mg/hr. The fuel cell plus human emission rates are limited to the 9 g/m^3, so the fuel cell emission rate is limited to 60,000 mg/hr. (Source: IEC 62282-6-1)
8. How are risks of buildup in the product enclosure of hydrogen and other flammable gases mitigated?	1. The product enclosure will have multiple vents throughout the product surface. Therefore, buildup of flammable gases will be very unlikely. 2. If flammable gas buildup were to occur from blocking of vents, the system will immediately shutdown from oxygen starvation. 3. Any flammable gas will be diluted by the presence of large amounts of cooling air and nonflammable exhaust gases (e.g., water, carbon dioxide, nitrogen from air). 4. The volume available for gas buildup is limited, since the enclosure will be fully occupied by product components. 5. The system is designed and tested to prevent flammable gas emission, including the maintenance of hydrogen emissions below 25% of the LFL. 6. The leakage of flammable gases, including hydrogen, would cause system cooling, as described in Items 3 and 4. Temperature is continuously monitored through redundant temperature sensors and shuts down under these cooling conditions. The system's microcontroller controls the system functions and will shutoff fuel and air delivery. 7. The microcontroller will also physically disconnect the fuel cartridge from system if there is this type of cooling. 8. Microcontroller failure automatically causes the fuel to shutoff.
9. What is done to mitigate the risk of a potential worst case scenario of hydrogen buildup, such as hydrogen emissions in a closed suitcase?	1. The catalytic heater will consume oxygen and cause system shutdown well before approaching a flammable mixture. 2. If the catalytic heater is not running, the system will immediate cool and shutdown. 3. The system is designed and tested so that the hydrogen content of exhaust gases never exceed 25% of the LFL. 4. Hydrogen, because of its small molecular size, is difficult to retain.

10. Do the reformer, fuel cell or catalytic heater catalysts present a risk?	1. RMFC catalysts do not present a danger. They are not pyrophoric or dangerously self heating materials. When the UN Division 4.2 test protocol for self-heating materials is applied to the amount of catalyst in an RMFC system, heating is minimal. Note that the UN Division 4.2 test protocol also calls for large amounts of material (a 1 L cube). However, this test is not applicable to RMFCs, since they contain approx. 100 times less material than this amount. 2. RMFC catalysts are not UN Division 4.3 water reactive materials, nor do they meet any other UN criteria for hazardous materials.
11. How are flammability risks of the fuel cartridge mitigated?	1. The fuel cartridge is physically separated from the reaction point and all high temperatures. This is a significant safety advantage of micro fuel cells. Several layers physically separate the cartridge from the high temperature inside the reformer: the reformer housing, the reformer insulation, internal system components, internal system cooling air, product enclosure, and cartridge housing. 2. The cartridge is maintained at ambient temperatures, and the fuel is in a liquid form. 3. The methanol fuel in the cartridge is far from the flammability and explosive range. The upper explosive limit of methanol is 36%, whereas the cartridge is well above 99% methanol-water fuel. The use of a fuel bladder combined with system design precludes air from mixing with methanol in the cartridge. 4. The cartridge does not contain ignition sources 5. The cartridge body, valve, and connect/ disconnect mechanism are designed and tested to prevent methanol release, as outlined below in Item 12.
12. How is methanol leakage from the fuel cartridge?	1. The fuel cartridge will be designed and tested to demonstrate its ability to maintain integrity with high internal pressures and loss in ambient pressure from high altitudes (>95kPa). 2. The fuel cartridge will be designed and tested to withstand extreme temperatures (-40^{o}C - 85^{o}C). 3. The fuel cartridge will be designed and tested to tolerate drop heights of 1.8 m, vibration (7 Hz - 200 Hz, 1 gn - 8 gn), crushing force of 100 kg. 4. The fuel cartridge components that are in contact with the methanol fuel will be designed and tested to tolerate exposure over product life and throughout product environment (temperature of -40^{o}C - 85^{o}C, pressure differentials of at least 95 kPa, humidity 0-100%).

	5. The fuel cartridge will be 3rd party certified (e.g., a UL product test lab) in accordance with IEC 62282-6-1.
13. Is pressure buildup a risk in the unit?	1. RMFCs are “open” systems. This means that the system is open to ambient pressure. This prevents flow channels from building up in pressure, regardless of the temperature.

Section 5. The IEC safety standard for micro fuel cells

This section provides an overview of the international product safety standard for micro fuel cells being prepared through the International Electrotechnical Commission (IEC).

What is the IEC safety standard for micro fuel cells, and what is its scope?

The International Electrotechnical Commission (IEC) is the electrical counterpart to International Standards Organization (ISO), and the standard (IEC 62282-6-1) is being finalized to ensure safe operation of micro fuel cells in all reasonable uses, including onboard commercial aircraft. The standard addresses RMFCs, among other micro fuel cell technologies and is currently being finalized for international review and comment. Final publication of the standard is expected by the end of 2006.

As outlined in the draft of the standard, its scope is:

> "This consumer safety standard covers fuel cell power systems and fuel cartridges that are wearable or easily carried by hand, providing DC outputs that do not exceed 60 V DC. SELV limits and power outputs that are ≤ 240 VA. As such, the external circuitry are considered circuits that are "SELV" as defined in IEC 60950-1, and are considered to be limited power circuits if further compliance with IEC 60950-1, Section 2.5 is demonstrated. Systems that have internal systems exceeding 60 V DC or 240 VA must be appropriately evaluated in accordance with separate criteria of IEC 60950-1."

What test requirements are covered by this safety standard?

IEC 62282-6-1 contains an extensive range of product safety tests, including: temperature cycling, altitude simulation, vibration, drop, compressive loading, short circuiting, surface temperature, exhaust temperature, long-term storage, internal pressure, and emission tests. Since RMFCs are methanol fuel cells, they will have very similar tests and criteria to DMFCs. In addition, RMFCs have tests requiring auto shutdown with abnormally high temperatures, safe operation under high temperatures, and hydrogen emissions tests (Annex C). The set of tests is designed to conform to all international requirements for commercial aircraft.

What is the process by which a micro fuel cell becomes IEC-certified?

The micro fuel cell manufacturer seeking recognition by the international transportation regulators would be required to sample systems and cartridges to a recognized 3rd party test lab (such as UL) for compliance testing and certification. The test lab would conduct all tests as specified in IEC 62282-6-1 and provide a test report. If the product complies, the certified product would carry a certification mark and other marking indicating compliance with IEC 62282-6-1.

Conclusion

RMFCs offer high levels of portable power safety. The user experiences low surface and exhaust temperatures, and the small amount of hydrogen within the system is only a process intermediate that is not dangerous to the user. The catalytic heater, furthermore, provides a robust means of ensuring conversion of all streams to a safe exhaust of carbon dioxide and water. The high temperature (280^{o}C) reformer is easily isolated with well known insulators, much like a microprocessor's temperature is isolated from the laptop user. RMFC catalysts are not hazardous materials. The system is open to ambient pressures and therefore does not have pressure buildup from high temperatures. RMFC fuel cartridges are designed to safely withstand all foreseeable stresses in transportation, and the cartridge is well isolated from the reaction point in the RMFC. Finally, the IEC Working Group 8 safety standard (IEC 62282-6-1) provides a rigorous testing for RMFCs, ensuring safe operation.

It is the proposal of the RMFC IEC Safety Task Group that RMFCs are considered along with DMFCs in the class of Methanol Fuel Cells and are approved for onboard usage by passengers on commercial aircraft. This approval will be a key step forward in the coming widespread commercialization of RMFCs as a safe and advanced form of portable power.

Appendix A: Examples of RMFC products

Figure 6. An UltraCell RMFC system for laptop computers

Figure 7. An UltraCell RMFC system for laptop computers

Figure 8. Image model of a Casio RMFC system for laptop computers

Appendix B: RMFC product safety working group contacts

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1. Incropera, Frank P., and Dewitt, David P. *Fundamentals of Heat and Mass Transfer*. 5th edition, p. 912. Wiley, 2001.
2. Motorola, Casio, and UltraCell test data.

Appendix B

RMFCs (Reformed Methanol Fuel Cells) Leakage definition and Type test items of Committee Draft by IEC/TC105 Micro Fuel Cell Safety WG8 (IEC-62282-6-1)

Additional Type Tests for RMFC micro fuel cell systems and fuel cell power units

Purpose : The type tests for RMFC micro fuel cell systems, fuel cell power units provide that these systems are safe for normal use.

The type tests for RMFC fuel cartridges are same as the fuel cartridges described in the main body of this standard.

Requirements : Most of type tests require "No leakage, no fuel vapor loss, no fire and no explosion"

Test Item	Purpose	Test sample	Test Conditions and Test Procedures	Requirements
All tests described for DMFC should be performed prior to the tests described in this page.				
1.Hydrogen emissions test*	To ensure safe emissions levels in 1 m^3 chamber.	After executing the type tests in accordance with the test procedure described in page 1, the same micro fuel cell power unit shall be used.	1) The Emission Test Apparatus should be made based on 1 m^3 ・ ACH (Example: 1m3 / 10ACH), wherein a mass spectrometer, gas chromatograph, or other suitable calibrated instrument is used. 2) It should be set up to monitor concentration of hydrogen within the control volume.	1) Hydrogen concentration is less than 0.0162 mg/hr (0.018% vol)**. This level would result from one single source venting pure hydrogen at 3cc/min***. If hydrogen concentration is less than 0.0162 mg/hr (0.018% vol), device passes leakage test. No further testing required. 2) If Hydrogen concentration is greater than 25% LFL. Device fails leakage test. No further testing required. 3) If Hydrogen concentration is greater than 0.0162 mg/hr (0.018% vol) but less than 25% LFL. proceed to the Hydrogen leakage test, summarized below.
2.Hydrogen leakage test	To ensure that there is no single point leakage of hydrogen that could support a flame.	After executing the Hydrogen emissions test, the same micro fuel cell power unit shall be used.	Sweep the entire surface of the micro fuel cell system with a hydrogen detector, ensuring no leakage rate is greater than 3 cc/min.	1) If no points are found where the hydrogen concentration is greater than 25% LFL, device passes the Hydrogen leakage test. 2) If any points are detected to have a hydrogen concentration of 25% LFL or greater, a second test must be conducted to ensure that the emission does not exceed 3cc/min*** of pure hydrogen from any single source.
3.Abnormal high temperature test	To ensure safe operation and automatic shutdown due to abnormaly high temperature	After executing the Hydrogen emissions test and Hydrogen leakage test, the same micro fuel cell power unit shall be used.	While the micro fuel cell power unit is operating at rated output; use the manufacturer's specified method for setting temperature to set a temperature 10oC above maximum operating temperature**** inside the reformer.	The system shutdown sequence is initiated within 5 seconds of the reformer reaching the temperature set point.
			1) Set the reformer temperature at 30oC above the maximum operating temperature****. 2) Disable the automatic system suspension mechanism (described in Section C.7.3.1.) 3) Run the system at full load as specified by the manufacturer for one hour at this elevated temperature.	There shall be no emission of flame, and the system shall be in compliance with emissions requirements in Table 7.3.13.1 and Section C.7.2.1.1.

* Hydrogen Emission Test — Hydrogen emissions and Hydrogen leakage test shall be done after each type test for a micro fuel cell power unit or power system is carried out.
(Pressure differential test -> Vibration test -> Temperature cycling test -> Emission test -> Hydrogen emissions test ->Hydrogen leakage test)

** 0.0162 mg/hr (0.018% vol) — This level of Hydrogen concentration would result from one single source venting pure hydrogen at 3cc/min.

*** 3cc/min — The IEC safety standard 62282-6-1 requires that the hydrogen emission rate is maintained at a very low level – less than 3 cc/min from a single source. This level was chosen because, under all circumstances, it is impossible for emitted gas to support a flame.

****maximum operating temperat — This value is specified by the manufacturer.

ICAO Member Briefing

Methanol Clathrate Compound as fuel for Direct Methanol Fuel Cells

ICAO DGP twentieth meeting in Montreal

Oct. 24－Nov. 4

Prepared by The Japan Electrical Manufacturers' Association (JEMA)

Table of Contents

1. Features of Methanol Clathrate Compound

1.1 What is "Methanol Clathrate Compound"?

Clathrate compound consists of host molecules and guest molecules (see figure 1). Guest molecules are present in cavities formed by crystal lattices and/or present in host molecules by interactions of host and guest molecules. Host and guest molecules in clathrate compound are not reacted, and they can separate by appropriate means. In case of the methanol clathrate compound (MCC), the guest molecule is methanol.

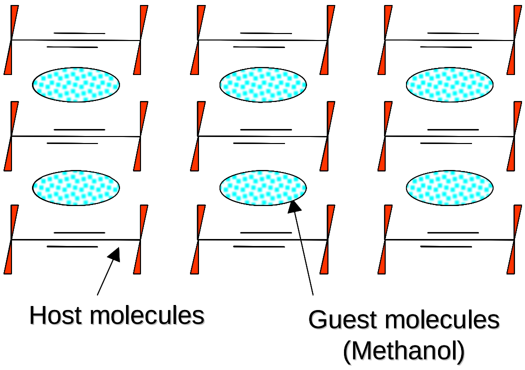

Figure 1 Crystal structure image of MCC.

1.2 Features of MCC

MCC is a solid-state material (see figure 2). The physical properties of methanol in MCC are quite different from pure liquid methanol. One of them is the vaporization rate. Because of the strong molecular interactions, the vaporization rate of methanol in MCC is quite lower than that of pure liquid methanol. By virtue of this feature, MCC is not classified as class 4 (Flammable solids, etc.) of "United Nations Classification Recommendation on Transport of Dangerous Goods".

Figure 2 Electron microscope photograph of MCC.

Methanol molecules in MCC are released not only by heating, but also keeping in contact with water. In case of using water, methanol is released as aqueous methanol solution.

1.3 Application of MCC as a fuel for Direct Methanol Fuel Cells

The characteristics of MCC as a fuel for Methanol Fuel Cells (MFC) are shown below.

(a) Improvement in safety

Since the MCC fuel cartridge contains only MCC before installing in MFC system, the leakage of liquid does not occur. Furthermore, the combustion risk of MCC is lower than that of methanol, and MCC doesn't come under any classes of "United Nations Classification Recommendation on Transport of Dangerous Goods".

(b) Compatibility of MCC to the MFC power unit

When the MCC fuel cartridge is used with the MFC power unit, the cartridge is installed in the MFC power unit, and water is supplied to the cartridge. Then methanol solution is formed by release of methanol from MCC to water, and it can be used as fuel for general DMFC power unit (see Figure 3).

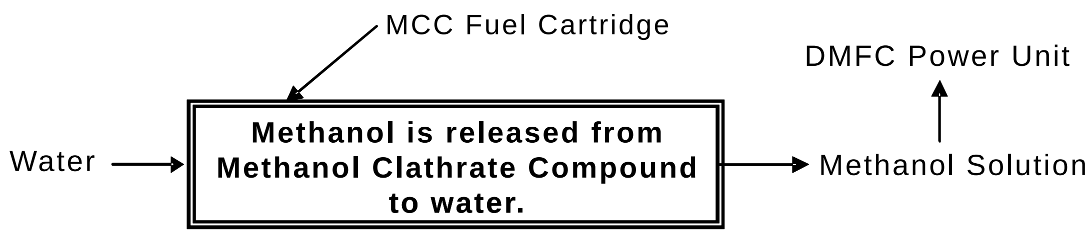

Figure 3 Usage of MCC with DMFC power unit

2. Safety properties of Methanol Clathrate Compound

2.1 Safety data of MCC ingredients

The ingredients of MCC are methanol and γ-cyclodextrin (γ-CD). As mentioned above, host molecules (γ-cyclodextrin) and guest molecules (methanol) doesn't reacted in MCC, so that the safety properties of MCC can considered as the mixture of γ-CD and methanol. Table 1 shows the safety properties of γ-CD and methanol.

Table 1 Safety properties of γ-CD and methanol.

Safety Items		γ-Cyclodextrin		Methanol	
		value	unit	value	unit
CAS No.		17465-86-0		67-56-1	
HMIS rating					
	Health	0		3	
	Fire	1		3	
	Reactivity	0		0	
Acute health contact					
	Eye contact	No acute toxic effects are expected.		Moderate irritant	
	Skin contact	No acute toxic effects are expected.		Irritant	
	Inhalation	No acute toxic effects are known.		Yes	
	Ingestion	No acute toxic effects are expected.		Yes	
	Additional information	In animal tests: not sensitizing.			
Further Information					
	Carcinogens	No		No	
	Reproductive toxins	No		20000	ppm (rat)
Flammable Properties					
	Flash point	-		11	℃ (TCC)
	Lower Explosion Limit	60	g/m3	6	vol%
	Ignition Temperature	450	℃	385	℃
Acute toxicity					
	oral (rat)	>8000	mg/kg	5600-13000	mg/kg
	skin (rat)	>2000	mg/kg	15800	mg/kg (rabbit)
	inharation (rat)	4.9	mg/L/4h	64000	ppm
Chronic toxicity					
	Rat Repeated dose: 90 day	>8270	mg/kg/h/d		
Exposure Limits					
	ACGIH TLV-TWA	10	mg/m3	200	ppm
	OSHA PEL	15	mg/m3	200	ppm
<<JECFA* >>					
	ADI (Acceptable Daily Intake)	Not specified (very low toxicity)		Limited by GMP**	

* JECFA: Joint FAO/WHO Expert Committee on Food Additives
** GMP: Good Manufacturing Practice

Table 1 shows that γ-CD is quite safer material than methanol. Exposure control of γ-CD at the workplace is established (ACGIH, 10 mg/m^3) as "Particulates not otherwise classified". This criterion is not based on the toxicity. It can be also understood that "Starch" is classified as the same particulates and the same criterion is applied.

Based on these data, it is concluded that the safety properties of MCC, which can be considered as the mixture of γ-CD and methanol, are better than that of methanol in the viewpoint of health and combustion risks.

2.2 UN Classification of MCC

By the properties of MCC and our results of tests provided in the UN Test Manuals, it is obvious that MCC is not subject to the UN Model Regulations, that is, MCC is not dangerous goods. MCC will be carried and distributed as a form of the fuel cartridge, and it can be also handled as non-dangerous goods because it contains only MCC.

Table 2 United Nations Classification Recommendation on Transport of Dangerous Goods.

Class	Division	MCC
1	Explosives	Not Classified
2	Gases	Not Classified
3	Flammable Liquids	Not Classified
4	Flammable solids, etc.	Not Classified (T)
5	Oxidizer	Not Classified
6	Toxic substances, Infectious substances	Not Classified
7	Radioactive Materials	Not Classified
8	Corrosive Substances	Not Classified (T)
9	Miscellaneous Dangerous Substances	Not Classified

(T): Confirmed by tests provided in the UN Test manuals.

3. Risk analysis of Methanol Clathrate Compound as fuel for DMFCs.

The risk analysis of MCC as a fuel for DMFCs is performed. The results are summarized in Tale 3.

Table 3 Risk analysis of MCC as fuel for DMFCs.

No.	Risk Description	Risk Mitigation
1	MCC solid is leaked from the fuel cartridge. 1) Toxicity 2) Flammability 3) Inhalation of dust	<Risk Mitigations> • The same safety criteria for liquid methanol (Any accessible leakage doesn't permitted) are applied to MCC because MCC contains methanol. • The safety criteria for MCC are described on Annex D in IEC 62282-6-1 (Micro fuel cell power systems - Safety) (See Chapter 4). This standard includes the requirements to ensure a reasonable degree of safety for normal use, reasonably foreseeable misuse, and consumer transportation of MFC power systems powered by MCC and MCC fuel cartridges. • Exposure control of γ-CD at the workplace is established (ACGIH, 10mg/m^3). This criterion can be satisfied by observance of the above safety criteria for MCC. <Comments> • MCC is safer than liquid methanol in respect of toxicity, combustion and leakage risk, so that potential risks can be reduced.
2	Methanol solution is leaked from the fuel cartridge 1) Toxicity 2) Flammability	<Risk Mitigations> • In case of the leakage of the methanol solution, which is generated by the contact of MCC and water, the safety criteria for liquid methanol are also applied. <Comments> • Although small amount of γ-CD is dissolved in the methanol solution, the risks of the methanol solution do not increased.
3	Methanol vapor is leaked from the fuel cartridge 1) Toxicity 2) Flammability	<Risk Mitigations> • In case of the leakage of the methanol vapor, the safety criteria for liquid methanol (<0.33 g/h as methanol vapor) are also applied. <Comments> • Because the vaporization rate of the methanol in MCC is lower than that of liquid methanol, the risks of the methanol vapor (combustion and inhalation) are abele to reduce.

4. Summary of the type test requirements concerning MCC

MCC fuel cartridge and DMFC systems powered by MCC are subjected to safety testing associated with the proposed IEC 62282-6-1 (Micro fuel cell power systems – Safety). A summary of the type test requirements concerning MCC is described in **Appendix A**.

5. Conclusion

- MCC is the only fuel for micro fuel cells that is a non-dangerous article in the form of the fuel cartridge. MCC improves the safety of the liquid methanol fuel in transportation, storage, distribution, and consumer's handling as the fuel cartridge.
- The safety can be secured by observance of the safety criteria similar to the liquid methanol because MCC contains methanol and has possibility to release methanol.
- The safety criteria concerning MCC are provided in detail by Annex D in IEC62282-6-1 (Micro fuel cell power systems – Safety). This standard includes the requirements for MFC power systems powered by MCC and MCC fuel cartridges to ensure a reasonable degree of safety for normal use, reasonably foreseeable misuse, and consumer transportation of such items.

Appendix A

MCC (Methanol Clathrate Compound) as fuel for DMFCs (Direct Methanol Fuel Cells) Leakage definition and Type test items of Committee Draft by IEC/TC105 Micro Fuel Cell Safety WG8 Leakage Definitions

<< Note: The under line parts are parts different from the safety standard of the methanol as fuel for DMFCs>>

1.NO LEAKAGE	No accessible hazardous liquid fuel outside the system or cartridge.
2.NO FUEL VAPOR LOSS	Fuel vapor escaping from the cartridge or system is less than 0.33 g/hr.
3.HAZARDOUS LIQUID FUEL	Any liquid fuel amount over 5 ml or a concentration of methanol greater than or equal to 4% by weight in water.
4.NO ACCESSIBLE LIQUID	Consumer cannot come into physical contact with HAZARDOUS liquid fuel.
5.NO MCC POWDER LEAKAGE	**No accessible MCC powder outside the system or cartridge.**

Type Tests

Purpose : The type tests for micro fuel cell systems, fuel cell power units and fuel cartridges provide that these systems are safe for normal use, reasonably foreseeable misuse, and consumer transportation.

Requirements : Most of type tests require "No leakage, **no MCC powder leakage**, no fuel vaporloss, no fire and no explosion"

Test Item	Purpose	Test sample	Test Conditions and Test Procedures	Requirements
1.Pressure differential tests*	To simulate the effects of a high internal pressure or low external pressure and ensure no leakage.	unused Fuel cartridge	1) An internal Pressurization or 2) Low External Pressure test shall be done. 1) >95 kPa gage pressure plus normal working pressure at RT*** or 2 times the vapor pressure of the fuel at 55 ºC for 30 minutes at room temperature. 2) 95 kPa differential applied for 30 minutes. (for a rigid cartridge)	1) Internal Pressurization No accessible liquid test medium leakage and no sudden drop of pressure. 2) Low External Pressure No fire at any time, no explosion at any time, no leakage, no **MCC powder leakage**, no fuel vapor loss.
		Micro fuel cell power unit or power system	Both 1) Test A and 2)Test B shall be done. 1) Test A : 68 kPa for 6 hours at RT. 2) Test B : 95 kPa differential pressure for 30 minutes at RT.	1) Test A No fire at any time, no explosion at any time, no leakage, no **MCC powder leakage**, no fuel vapor loss. 2) Test B fuel vapor loss less than 20g/hr
2.Vibration test*	To simulate the effects of normal transportation vibration and ensure no leakage.	unused Fuel cartridge and Micro fuel cell power unit or power system	7 Hz (peak acceleration of 1 gn) and 200 Hz (peak acceleration of 8 gn) and back to 7 Hz traversed in 15 minutes. This cycle shall be repeated 12 times for a total of 3 hours for each of three mutually perpendicular	No fire at any time, no explosion at any time, no leakage, no **MCC powder leakage**, no fuel vapor loss.
3.Temperature cycling test*	To simulate the effects of low temperature and high temperature exposure and the effects of extreme temperature change.	unused Fuel cartridge and Micro fuel cell power unit or power system	-40 C 4 hours to 55 ºC 4 hours 2 times	same as above
4.High temperature exposure test	To simulate the effects of a fuel cartridge left in high temperature environments.	unused Fuel cartridge	70±2ºC for 4 hours	same as above
5.Drop test	To simulate the effects of an inadvertent drop and ensure no leakage.	unused Fuel cartridge and Micro fuel cell power unit or power system	The test sample shall be dropped on the horizontal surface consists of hardwood 1.from 120 cm in hight for a fuel cell power unit or system 2.from 180 cm in hight for a fuel cell cartridge The drop shall be carried out towards 4 directions(valve up, valve down and two other mutually perpendicular dorections.	same as above
6.Compressive loading test	To simulate the effects of the forces reasonably encountered due to being stepped on or something heavy being placed on the fuel cells	unused Fuel cartridge and Micro fuel cell power unit or power system	1. 25 kg for 5 sec. : A fuel cell power unit or system 2. 100 kg for 5 sec. : A fuel cell cartridge	same as above
7.External short-circuit test	To simulate the effects of an external short circuit.	Micro fuel cell power unit or power system	0.1 ohm for at least 5 minutes	same as above
8.Surface and exhaust gas temperature test	To eliminate any risk of burn injury caused by contact with the enclosure of fuel cell power system or blown exhaust gas from the vent.	Micro fuel cell power unit or power system	1.To measure the temperature of the bare surface of micro fuel cell power units and/or micro fuel cell power systems operating at rated output. 2.To measure the temperature of exhaust gas within 1 cm of the exhaust vent of micro fuel cell power units and/or micro fuel cell power systems operating at rated output.	No burn (The maximum temperature at the casing surface shall not exceed the specified values depending upon the material which are shown in Table4.18.1 of IEC-62282-6-1safety standard. The temperature at 1 cm of the exhaust vent of operating micro fuel cell shall be less than 70 ºC.)
9.Long-term storage test	To simulate the effects of long term storage at elevated temperature upon a fuel cell cartridge and ensure no leakage.	unused Fuel cartridge	50ºC for 28 days	No fire at any time, no explosion at any time, no leakage, no **MCC powder leakage**, no fuel vapor loss.
10.High temperature connection test	To simulate the effects of mating and un-mating of the fuel cartridge to the fuel cell power unit at an elevated temperature and ensure no leakage, no fire, no explosion.	unused Fuel cartridge and Micro fuel cell power unit	The test cartridge is kept in the chambercontrolled at temperature of 50±2ºC for 4 hours. And the test FC power unit is kept at RT.	No fire at any time, no explosion at any time, no leakage, no **MCC powder leakage**.
11.Fuel cell power unit internal pressure test	A) To test those parts of the fuel cell power system that maintain a high fuel pressure during operation or storage such as the sections between the cartridge and the system including the regulator valve or fuel pump or whatever is subject to a high pressure.	Micro fuel cell power unit or power system using pressurized cartridge	>95 kPa plus normal working pressure or two times fuel vapor pressure at 55ºC for 30 minutes.	No accessible liquid test medium leakage. No sudden drop in pressure.
12.Connection cycling test****	To simulate the effects of mating and un-mating of the fuel cartridge to the fuel cell power unit and ensure no leakage.	unused Fuel cartridge and Micro fuel cell power unit or power system	Fuel cartridges shall be repeatedly mounted on and dismounted from micro fuel cell power unit specified repetition cycles. 1.For a fuel cell power unit:thousand (1000) cycles desorption. 2.For a fuel cartridge except satellite cartridge: a minimum of ten (10) cycles desorption. 3.For a satellite fuel cartridge: a minimum of fifty (50) cycle desorption.	No fire at any time, no explosion at any time, no leakage, no **MCC powder leakage**.
13.Emission Test**	To ensure safe emissions levels of all possible emissions, under storage or operating conditions.	Micro fuel cell power unit or power system	To measure the concentration of emission gas from a fuel cell power system operating at rated power.	For a 1 m^3 chamber at 10 air change per hour (ACH).Emissions limits are as follows: Methanol: 2600 mg/hr, CO: 290 mg/hr, CO^2: 60000 mg/hr, Formaldehyde: 0.6 mg/hr, Formic Acid: 90 mg/hr, Methyl formate: 2450 mg/hr

* Sequential Test	For a fuel cartridge, Vibration test and Temperature cycling test shall be done sequentially (Vibration test -> Temperature cycling test)
	For micro fuel cell power unit or power system, Pressure differential test, Vibration test and Temperature cycling test shall be done sequentially (Pressure diffrential test -> Vibration test -> Temperature cycling test).
** Emission Test	Emission test shall be done after each type test for a micro fuel cell power unit or power system is carried out.
*** RT	Room temperature 22±5 ºC
**** Connection cycling test	As for a detail process, refer to 7.3.12 of IEC-62282-6-1safety standard.