DURAMET Methanol fuel Cells

SEVENTH FRAMEWORK PROGRAMME

New Energy World JU fuel cells & hydrogen for sustainability

Improved Durability and Cost-effective Components for New Generation Solid Polymer Electrolyte Direct Methanol Fuel Cells

Collaborative Project - *FCH JU Grant Agreement n° 278054*
SP1-JTI-FCH.2010.4.4 Components with advanced durability for Direct Methanol Fuel Cells
***Start date**: 01.12.2011 – **Duration**: 36 months*
***Project Coordinator**: Antonino Salvatore Aricò – CNR-ITAE*

DELIVERABLE REPORT

D2.1– Protocols for ex-situ characterisation of membranes	
Due Date	29.02.2012
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Dissemination Level		
PU	*Public*	***X***
PP	*Restricted to other programme participants (including the Commission Services)*	
RE	*Restricted to a group specified by the consortium (including the Commission Services)*	
CO	*Confidential, only for members of the consortium (including the Commission Services)*	

Nature of the Deliverable		
R	*Report*	***X***
P	*Prototype*	
D	*Demonstrator*	
O	*Other*	

SUMMARY	
Keywords	Specifications, Protocols, Membrane, DMFC
Abstract	The objective of this deliverable report is to define characterisation and test protocols for the assessment of performance, enhanced durability and cost-effective characteristics of the newly developed DMFC membranes.

REVISIONS			
Version	**Date**	**Changed by**	**Comments**
0.1	16.February.2012	M. Schuster	First draft
0.2	01.March.2012	A. Aricò	In-situ tests
0.3	13 March 2012	D. J. Jones	Membrane conductivity and dimensional change at 60-120 °C

D2.1– PROTOCOLS FOR EX-SITU CHARACTERISATION OF MEMBRANES

This deliverable defines a set of characterisation and testing protocols for an ex-situ characterisation of baseline and novel DMFC membranes to allow for a comparison of characterisation data within the project and to external sources, and to allow for a homogeneous screening and evaluation of the newly developed membranes. The deriverable identifies a benchmark membrane against which progress will be assessed in terms of properties. The protocols will be used as means of verification to assess the achievement of project milestones.

The characterisation protocols will be divided into a priority list that includes the minimum required properties of membranes for further evaluation, and a second list including a wider range of characterisation protocols. The priority list contains general aspects such as solubility, swelling and handleability under standard conditions. The second list defines characterisation protocols for membrane properties in more detail.

I. Baseline (benchmark) membrane

Baseline (benchmark) membrane will be Nafion 115 (DuPont).

In some experiments Nafion 117 can be also used.

II. **Priority list - General aspects**

The priority list provides general aspects for membrane evaluation such as solubility, swelling and handleability as minimum required properties of membranes for further evaluation.

- solubility test in water and in water / methanol at T = 25 °C
    - sample must not dissolve or swell excessively
    - no leach-out of functional groups (control by IEC measurement)
- handleability in dry and wet state
    - sample must not break when bent

III. Second list - Characterisation data under standard conditions

The second list provides characterisation protocols under standard conditions (T = 25 °C) with respect to the following membrane properties:

- Polymer type, reinforcement and appearance (colour)
- Ion exchange capacity
- Conductivity
- Thickness
- Uptake of solvent (water / methanol)
- Dimensional swelling (x-, y-, and z-direction)
- Methanol permeability
- Mechanical properties
- Thermal / thermo-oxidative stability (TGA)
- Glass transition temperature (DMA)

As one project target is the increase of methanol concentration, measurements in water - methanol mixtures will be carried out in 10 M methanol solutions.

Pretreatment of the membrane before measurement:

The membranes should be acidified before characterisation according to the following prescription:

- 1 M H_2SO_4 at T = 80 °C for 5 hours
- rinse in demineralized water
- store in demineralized water

IV. Third list – Conductivity determination and dimensional swelling at higher temperatures

Conductivity

Since the project targets both low (ambient-60 °C) and high temperature (120 °C) DMFC application, determination of the conductivity at these temperatures is required. Following membrane pre-treatment according to the protocol outlined above, the membranes should be placed in the conductivity cell (in-plane or through-plane) and allowed to equilibrate at the desired temperature and relative humidity. Conductivity measurement at full humidification is required and, in addition, it is recommended to determine the influence of relative humidity on the conductivity at 120 °C.

Recommended conditions are:

Ambient, 40, 60 °C at 95% rH

120 °C at 25, 50, 75, 95 % rH

Dimensional swelling

The increase in membrane dimension (x, y, z directions) on immersion (4 h) in water and aqueous methanol solutions (1, 2, 10 M) should be determined at 60 and 120 °C (e.g. in a closed glass or plastic bottle).

Table of characterisation data

	unit	membrane	method
polymer type			
batch No			
reinforcement			
appearance (colour)			
IEC (ion exchange capacity)	meq g^{-1}		method 1
EW (equivalent weight)	g eq^{-1}		method 1
thickness (dry)	µm		method 2
solvent uptake Δm in H_2O at 25 °C	wt %		method 3
in H_2O / MeOH at 25 °C	wt %		
in MeOH at 25 °C	wt %		
thickness increase Δz in H_2O at 25 °C	%		method 4
Thickness increase Δz in H_2O at 60 °C	%		
Thickness increase Δz in H_2O at 120 °C	%		
in H_2O / MeOH at 25 °C	%		
in H_2O / MeOH, 60 °C (1, 2, 10M)	%		
in H_2O /MeOH, 120 °C (1, 2, 10M)	%		

in MeOH at 25 °C	%		
MD increase Δx in H_2O at 25 °C			method 5
MD increase Δx in H_2O at 60 °C	%		
MD increase Δx in H_2O at 120 °C	%		
in H_2O / MeOH at 25 °C			
in H_2O / MeOH, 60 °C (1, 2, 10M)	%		
in H_2O /MeOH, 120 °C (1, 2, 10M)	%		
in MeOH at 25 °C			
TD increase Δy in H_2O at 25 °C			method 6
TD increase Δy in H_2O at 60 °C	%		
TD increase Δy in H_2O at 120 °C	%		
in H_2O / MeOH at 25 °C			
in H_2O / MeOH, 60 °C (1, 2, 10M)	%		
in H_2O /MeOH, 120 °C (1, 2, 10M)	%		
in MeOH at 25 °C			
conductivity in H_2O at T = 25 °C	mS cm^{-1}		method 7
area resistance in H_2O at T = 25 °C	Ω cm^2		
conductivity at T = 60 °C, 95% rH (specify through-plane or in-plane measurement)	mS cm^{-1}		
conductivity at T = 120 °C, 25% rH (specify through-plane or in-plane measurement)	mS cm^{-1}		
conductivity at T = 120 °C, 50% rH (specify through-plane or in-plane measurement)	mS cm^{-1}		

conductivity at T = 120 °C, 75% rH (specify through-plane or in-plane measurement)	mS cm^{-1}		
conductivity at T = 120 °C, 95% rH (specify through-plane or in-plane measurement)	mS cm^{-1}		
methanol permeation [d)]	Mol h^{-1} m^{-2}		method 8
Young's modulus at 23 °C / 50 % r.h.	MPa		method 9
tensile strength at 23 °C / 50 % r.h.	MPa		method 9
elongation at break at 23 °C / 50 % r.h.	%		method 9
start of thermal decomposition	°C		method 10
glass transition temperature T_g	°C		method 11

Description of characterisation methods

Method 1	IEC Determination	treatment of membrane sample with 0.1 M NaCl at RT for 12 hrs titration of solution with 0.1 M NaOH
Method 2	thickness	t.b.d
Method 3	solvent uptake	treatment of membrane sample in solvent at 25 °C for 1 hr removal of solvent from surface by tissue paper measure weight dry sample in vacuum over P_2O_5 at 50 °C measure dry weight
Method 4	thickness increase	treatment of membrane sample in solvent at 25 °C for 1 hr removal of solvent from surface by tissue paper measure thickness dry sample at room temperature and 50 % r.h. measure thickness
Method 5	MD increase MD = machine direction	treatment of membrane sample in solvent at 25 °C for 1 hr removal of solvent from surface by tissue paper measure membrane length in MD dry sample at room temperature and 50 % r.h. measure membrane length in MD
Method 6	TD increase TD = transverse direction	treatment of membrane sample in solvent at 25 °C for 1 hr removal of solvent from surface by tissue paper measure membrane length in TD dry sample at room temperature and 50 % r.h. measure membrane length in TD
Method 7	conductivity	in-plane / 4-electrode set-up membrane in demineralized water at 25 °C ac impedance
Method 8	methanol permeation	concentration cell: chamber 1: 1.0 M methanol chamber 2: demineralized water at T = 50 °C
Method 9	methanol permeation	concentration cell: chamber 1: 10.0 M methanol chamber 2: demineralized water at T = 50 °C
Method 10	stress-strain	European Standard EN ISO-527-1 to EN ISO-527-3 speed 0.25 mm/min
Method 11	TGA	T = RT to 900 °C air or nitrogen atmosphere heating rate 2 °C/min
Method 12	DMA	T = RT to 400 °C in air heating rate 2 °C/min frequency 1 Hz T_g at maximum of tan(δ)

Further characterisation protocols under conditions related to project targets for both APU applications (120 °C target) and portable applications (60 °C target) will be specified in a further step. This will include swelling, conductivity and methanol permeation measurements in water and water - methanol at elevated temperatures up to 120 °C. This may also include DMA in water and water / methanol mixtures at various temperatures.

Although this deliverable is regarding ex-situ membrane characterization, some in-situ characterization dealing specifically with the membrane properties is here anticipated and it will be further addressed in D2.3.

In-situ conductivity measurements will be carried out at various temperatures and operating current densities by using the ac-impedance spectroscopy method. The series resistance determined by the high frequency intercept on the real axis of the Nyquist plot will be used to determine the ohmic resistance. This will be subtracted by the resistance contribution of electrodes and hardware measured in a separate test. The conductivity will be thus determined by normalising the results by the membrane thickness and electrode area according to the general formula. This approach will allow getting information about the conductivity under real operating conditions. It will provide interface resistance assessment by comparing the values determined in situ under OCV with those measured ex-situ. In situ conductivity will be measured as a function of the operating current density (this influences the electro-osmotic drag) and in the presence of different methanol solutions. For a proper comparison of the in situ data, it will be necessary to report all operating conditions including temperature, reactants, cathode humidification, and pressure for both compartments and operating current density.

Protocols for in situ methanol cross-over measurements will be defined in the deliverable dealing with MEA characterization (D2.3). The data will be reported both in terms of methanol permeation as mmoles CH_3OH per min per cm^2 (milestone MS3) as well as in terms of equivalent cross-over current density.

The selectivity calculated as the ratio between conductivity and methanol cross-over (mS min. cm mol_{met}^{-1}) will be used as a relevant parameter for membrane screening.

A representative table regarding in-situ membrane characterization is reported below:

Membr.	Cell Temp. °C	Cathode Humid. R.H.%	Anode Feed (methanol solution) M	Cathode feed (O_2/air)	Pressure Anode/ Cathode bar abs.	Operating Current Density $mAcm^{-2}$	Conduct. mS cm^{-1}	Methanol Cross-over $mol_{met} min^{-1} cm^{-2}$	Selectivity mS min. cm mol_{met}^{-1}