SMALLINONE

227177-2

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CEA/LITEN

SmAllInOne strep FP7,
program theme NMP4 energy
From April 2009 to March 2012

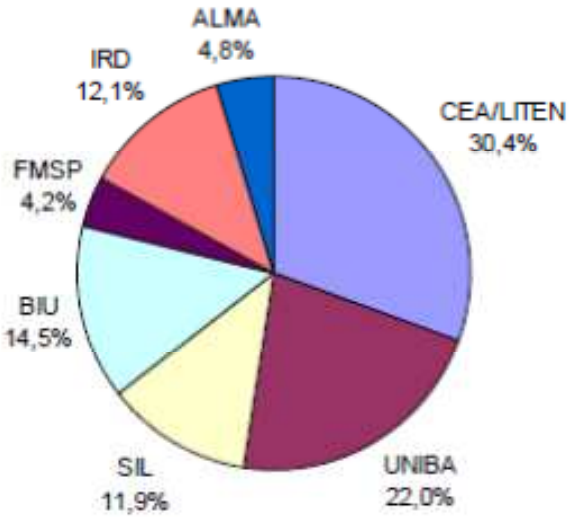
Objectives

- Realization of fuel cells via vacuum techniques
- Innovative architecture (incorporation of the catalytic functions in the ionic membrane)
- Incorporation of smart functionalities in the membrane (electronic conductivity, hydrophilic functions)

Challenges regarding the SoA

- Synthesis of volatile precursors
- Deposition of ionic membranes via vacuum techniques
- Two ≠ processes in the same tool
- Power outputs targeted with ultra low Pt load *(1W/cm^2 with Pt load <0.1mg/cm^2)*
- Compatibility of the process as well as that one of material with the Roll to Roll flexible substrates

Budget: 2 416 723 euros
Grant: 1 825 000 euros



Grant
public : 66.9%
private : 33.1%

1. Project achievement
WP1: Nanoprecursors synthesis / M1-18

WP/task 1.1-1.2: synthesis of

- precursors – M1-30 (UNIBA/BIU)
- UNIBA identification of *novel polyfluorinated*

sulfonic-type plasma precursors = quite good volatility and stability = Film basis for plasma deposition and post chemical modifications (*methyl sulfonate* & *persilylated type* hydrolysis)

- Provision of an original persilylation protocol for polar sulfonate/carboxylate/phosphonate plasma precursors using one unique neutral $SiMe_3$ group transfer reagent *dimethylketene methyl trimethylsilyl acetal – positive monomer plasma deposition*
- *Both plasma monomer approaches are breakthrough innovative in the field (extensive literature searches – SciFinder Scholar, CAS databases)*

WP/task 1.3: Synthesis of hydrophobized hybrid SiO_2 nanoparticles - M19-36 (BIU)/*Task replacement by the new one:* Conductive Pt-Based Nanomaterials for Fuel Cell Catalysis - M19-36

- Validation of a new concept based on the benzophenone-activated photo-reduction of Pt^{4+} cations – Use of a UV-reactive photoreactive silane **BPhTES** for the fabrication of biphasic Pt NPs-containing conductive particles as **new fuel cell *non-carbon*-based catalysts**
- Using this innovative generic method, realization of Pt/WC Pt/WO_3 and Pt/ATO NPs systems

1.Project achievement WP/T2.1: advanced membrane synthesis / M1-18

- UNIBA identification of novel iCVD process for the deposition of sulfonyl fluoride membranes with *conductivities as high as 60mS/cm* and deposition of carboxylic and sulfonic membranes by plasma CVD
- CEA development of carboxylic and sulfonic membranes by plasma CVD – *conductivities between 20 to 200mS/cm*
- SIL – carboxylic membrane via the ASPD technique – *conductivity 160mS/cm*

Material	***Method***	***conductivity***	***Observation***
sulfonic fluorocarbon - CEA	PECVD from PSEPVE	20mS/cm	Transparent coating, R~5-10nm/min, Water immersion 1H, 90°C: no degradation of the membrane
Carboxylic fluorocarbon -CEA	PECVD from C_4F_8 and water	30-200mS/cm	Braun coating , R~50-200nm/min The films with the highest conductivity are damaged in water
carboxylic fluorocarbon -UNIBA	PECVD from acrylic acid/C_3F_6	10-70 mS/cm	Brawn coating, R~20-60 nm/min Films from pure AA at high W stable in water (1h at 90°C)
CFS (sulfonic fluorocarbon membrane) UNIBA	iCVD from PSEPVE	60 mS/cm	Transparent coating /R~25 nm/min Films stable in water at 37 °C under hydrolysis
Carboxylic fluorocarbon membrane - UNIBA	iCVD from MAA+PFDA	40-70 mS/cm	Transparent coating / R~ up to 500 nm/min Films are stable in water
ASPD - SIL	From acids	160mS/cm	no cracks and no dissolution in water

Milestone R1: conductivity superior to 100mS/cm - ☺

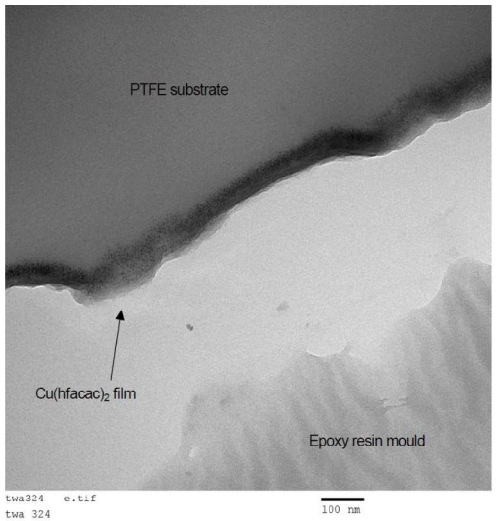
1. Project achievement
WP/Tasks 2.2 : percolated catalytic network - M1-18

- UNIBA sputtering of platinum nanoparticles in a CH_x or CF_x plasma CVD deposited matrix : UNIBA developed a methodology for depositing nano composite films based on a one step plasma process, where the relative contribution of plasma polymerization with respect to platinum sputtering is controlled by pulsing the monomer flow rate
- CEA deposition of C/Pt clusters using a Metal Organic Chemical Vapour Deposition method, very good NPs dispersion, high roughness factor
- SIL – metallic nanoparticles embedded in a polymer matrix

Material	*Method*	*Pt load*	*Roughness Factor*
UNIBA	Sputtering of Pt in plasma deposited matrix	**Between 0.07 and 0.2 mg/cm²**	**Between 8 and 32 cm²/cm²**
CEA	Metalorganic CVD	from 0.06 mg.cm^{-2} to 0.2 mg.cm^{-2}	Surface active 50cm²/cm² to 105cm²/cm²
SIL	Metalorganic CVD	In progress	In progress

Milestone R1: specific surface area > 100m²/g and Pt content < 0.1mg/cm² 😐 / partial

- UNIBA: the relative contribution of plasma polymerization with respect to platinum sputtering is controlled by pulsing the monomer flow rate. In order to deposit the Allinone material the reactor was implemented with a magnetron sputtering to functionalized the membranes with Pt nanoparticles. A shutter allows for protection of the target from poisoning during the pure membrane deposition.
- CEA found that both the catalytic and the membrane process can be operated at a moderate temperature of 200-250°C using the Plasma Enhanced MOCVD. The MOCVD reactor was implemented with a RF source. The relative contribution of polymer vs platinum is adjusted via the injection parameters.
- SIL : Low T PE-MOCVD from copper acac: control of the metallic cluster incorporation via the plasma discharge for a graded Incorporation



TEM image of copper(II) hexafluoroacetylacetonate film depositedat 5 W plasma power on a PTFE substrate

Milestone R2: indication of AllinOne Assembly with an OCV superior to 500mV- M18 : ☺

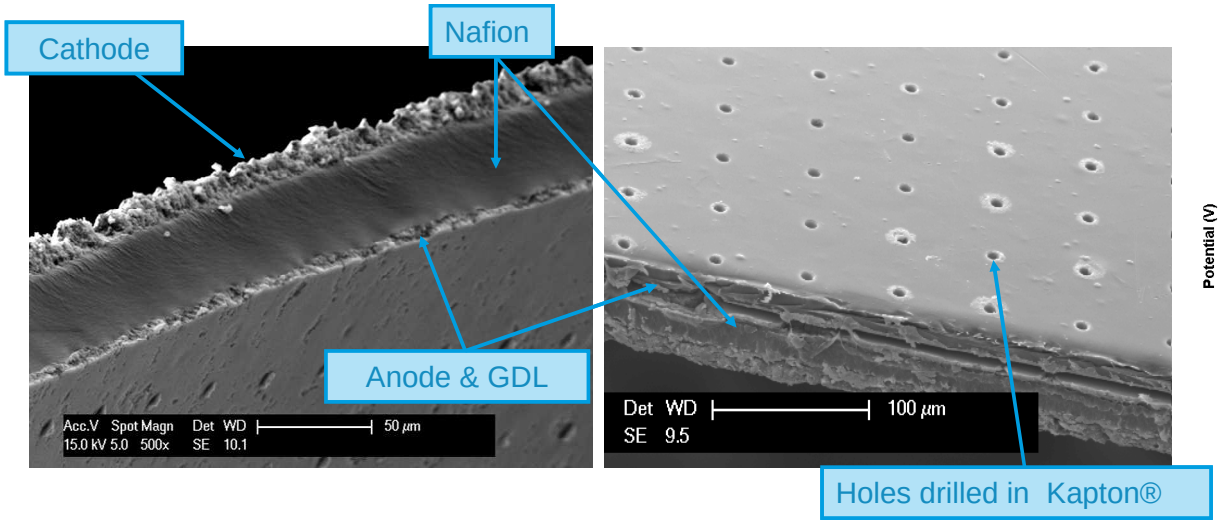
1.Project achievement WP/Tasks 5.2 : specific characterization for the AllinOne concept - M1-18

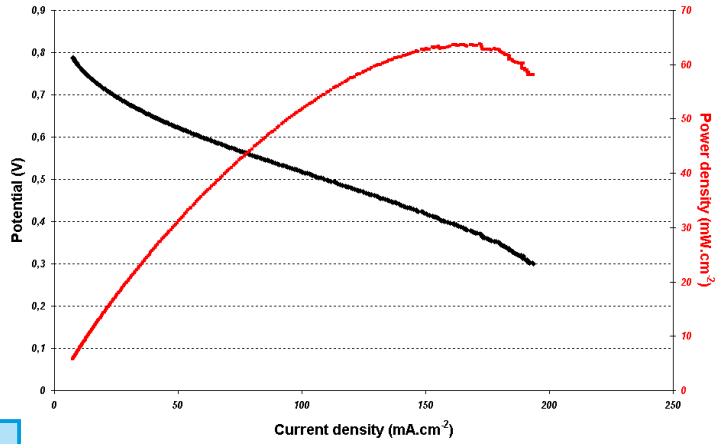
This AllinOne material is particularly suitable for miniaturization of the fuel cells interconnections provided the corresponding compatible supports and a micro-porous layer can be found. These supports must be insulating, low cost, with a localized porosity. The micro-porous layer with the substrate must be porous enough to let high hydrogen supply. In this light, CEA developed porous flexible substrates by laser drilling polyimide foils.

→ FC power densities as high as 65mW/cm^2 in breathing configuration

→ Compatibility with temperature deposition as high as 350°C

→ Open the possibility to use the PCB-like interconnection technologies to lower the fabrication costs



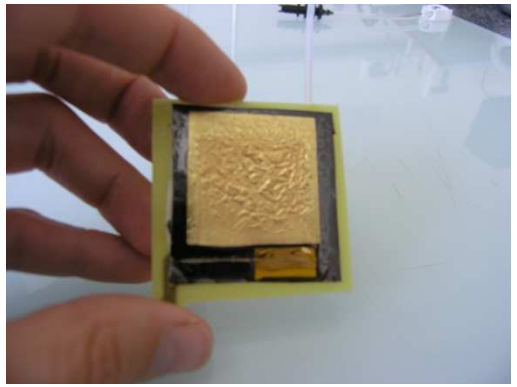


Ionic membranes developed within SmallinOne:

- carboxylic materials need enhancement of the cross-linking to be used as membrane
- Open circuit voltage as high as 900mV for the iCVD and PECVD sulfonic coatings
- AllinOne catalyst, breathing conf.: 50mW/cm^2
- AllinOne catalyst at the cathode, single cell conf.: 140mW/cm^2

Milestone R3: Optimized AllinOne OCV superior to 800mV : ☺ and power density of the order of 100mW/cm^2 : ☹

- Delay for the first AllinOne materials
- Ultra-low thicknesses of deposited membranes pose challenges
- Integration of vacuum deposited membranes is not trivial
- Performance evaluated against the very low platinum loadings



Future

- Optimization of the integration for improved power outputs
- Catalysts AllinOne optimization

With respect to the

MAIP document, the SmallinOne project addresses

- the early market's FC: The project proposes a top down integration via the realization of the membrane electrode assembly using vacuum techniques. The proposed architecture uses the techniques coming from micro-electronics, for the deposition of the various layers composing the active parts of the cell. This integration is particularly suitable for miniaturization of the fuel cells interconnections. Impacts are the possibility to realize fuel cells via microelectronic techniques.
- But also with the development of new catalytic materials, the project may adresses the Stationary Power Generation & Combined Heat Power (CHP). Expected impacts could be the improvement of the performances vs ageing.

RTD&D proposed by MAIP/AIP documents:

- Early market / portable FC –call SP1-JTI-FCH.2011.4.4 and 4.5: only 50W-500W systems; problematic of FC integration / architecture not underlined whereas it is crucial for very low power systems.

• Training & Education:

Contributed to the scientific formation of ***three*** (2BIU – 1UNIBA) ***PhD students*** and of ***three*** (2BIU -1CEA) ***post-doctor*** and of ***one engineering student (IRD)***
Cooperative connectivity between BIU / UNIBA / CEA students with other academic and industrial (IRD) partners = greater awareness of the way to conduct high-level industrial-related cooperation
CEA: Lesson on innovative micro fuel cells at the INSA school of Lyon

• Dissemination & public awareness

CEA&UNIBA patented the catalysts structure (US2011/0217628 A1 – September 8th, 2011) and an associated FC architecture (CEA patent application DD12047 (August 27th, **2010**). CEA already published the results on the carboxylic membranes J. Thery, S. Martin, D. Truffier-Boutry, A. Martinent, *Journal of Power Sources*, *Volume 195, Issue 17*, *1 September 2010*, *Pages 5573-5580*

The BIU original discovery on the photoreductive process for the fabrication of conductive non-carbon-based fuel cell catalysts has been patented (US Provisional Patent Application n° 61/193,447 (March 28th, **2011**) and published A. Peled, M. Naddaka, and J.-P. Lellouche, Smartly designed photoreactive silica nanoparticles and their reactivity, *J. Mater. Chem*, **2011**, *21*, 11511-17

Publication are expected:
CEA one publication is identified on the synthesis of sulfonyl fluoride membranes by PECVD and another on the realization of FC on laser drilled plastic foils
UNIBA expect three publications in journal such as the Journal of Applied Physics
BIU intend to publish the photoreactive reduction process in Angew. Chem. Int. Ed. Engl.

various conferences: International Conference on Plasma Processes and Applications, (J.P.Badyal), 240th American Chemical Society (ACS) National Meeting (JP. Badyal), Fondamental and development on fuel cells (J. Thery) …

Technology Transfer / Collaborations

The background knowledge utilised in the project has been acquired through research and development within the partners' various previous and on-going projects and collaborations with national and international private and public partners

Evaluation of the needs for FC membrane production and compatibility with FMSP industrial production strategy

The innovative FC catalyst concept will be ***one core part*** of a current BIU call for proposals of **the Israeli Ministry of Science** for the next 5 years-long cycle of establishment & funding of Israeli nanotechnology centers (INNI/Israel Nanotechnology Initiative/MOS/VATAT auspices (***Expected BIU funding of $ 45M in case of successful retained application)***

Contact and future collaboration with other university / research center and SME

Possible licensing of technology rights between partners in order to exploit commercial potential

 # photoreduced Pt-containing non- carbon-based FC catalysts (BIU→IRD)

 # vacuum deposited catalysts / membranes (CEA, SIL, UNIBA→IRD)

Proposed future research approach and relevance

High expectation to submit a contribution to the future FCH JU program or Member State national programmes

In the context of the development of *innovative photoreduced Pt-containing non-carbon-based FC catalysts (BIU core WP1 activities)* will be exploited via submission for a novel large/medium-scale EU VIIth framework cooperative project in the field in “NMP/Sustainable energy/green energy” domains – on-going work with part of the Small In One partners

Launching the unique and innovative SMAllinOne concept for further development within the frames of the FCH JU Programme

Next calls, CEA will submit a proposal in the AA “demonstration project” : SmallinOne FC architecture coupled with storage solution of the ISH2sup project, demonstration project, consumer tests – on - going work with part of the Small In One partners

Thank you