

international discussion on hydrogen energy and applications

02 - 04
NOVEMBER 2016
NANTES, FRANCE



HYDROGEN PRODUCTION AND STORAGE
SOLID OXIDE AND PROTON EXCHANGE
MEMBRANE FUEL CELLS AND ELECTROLYSERS:
FROM MATERIALS TO SYSTEMS

CHAIR : OLIVIER JOUBERT

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PROGRAM

WELCOME TO IDHEA 2016

>> *Message from the Chair*

Dear Participants,

Following the successful 2014-International Discussion on Hydrogen Energy and Applications (IDHEA) meeting, we are pleased to welcome you to the 2016- edition. The conference will take place on 2-4 November 2016 in the Congress Center "La Cité" located in the city center of Nantes on the west coast of France near the famous Loire Valley.

Blending fundamental research with practical applications in the field of hydrogen production, storage technologies, fuel-cells and systems is the main objective of this series of meetings.

Since the national organization committee of IDHEA 2016 is the CNRS Research Grouping called "HYSPAC" (www.gdr-hyspac.cnrs.fr and @gdr_hyspac) bringing together all of the French research communities working on hydrogen and fuel cells, the second objective of IDHEA is to blend leading scientists coming from around the world with the French HYSPAC network to share their recent progress and stimulate discussions on interdisciplinary Hydrogen technologies research and development.

During the 3-day program, more than 50 papers will be presented offering contributions from France and the international community. IDHEA will give academics, industry experts and politics the opportunity to present their most recent results through oral and poster presentations.

The scientific and industrial program of the conference will cover the topics:

- Production and storage of hydrogen
- Solid Oxide Fuel cells and Electrolysers
- Proton Exchange Membrane Fuel cells and Electrolysers
- Fuel cells and Electrolysers Systems

We would like to warmly thank the members of IMN, the French Research grouping "HySPàC" organizational teams for their involvement. Thanks are also given to the Scientific Committee for the high-level scientific program elaboration, the conference chairs, the invited and all speakers for their contribution for the success of this Conference.

Olivier JOUBERT (IMN, Director of HySPàC)

CONTENT

Program Outline	1
Committees	1
Conference Center Map	3
Detailed Program	
Wednesday, 2 nd November, 2016	5
Thursday, 3 rd November, 2016.....	8
Friday, 4 th November, 2016.....	11
Posters	13
ABSTRACTS	15

PROGRAM OUTLINE

	Wednesday, November 2, 2016	Thursday, November 3, 2016	Friday, November 4, 2016
08:00	Registration		
09:00	Opening Session		
09:30	Plenary	09:30 Keynote	09:30 Solid oxide Fuel Cell and Electrolysers
10:15	hydrogen production	10:00 Solid oxide Electrolysers	10:40 Coffee break
10:55	Coffee break	10:40 Coffee break	11:20 Solid oxide Fuel Cell and Electrolysers
11:25	Keynote	11:20 Solid oxide Electrolysers	13:00 Lunch and Coffee
11:55	hydrogen storage	13:00 Lunch and Coffee	14:00 Materials for hydrogen storage and transformation
13:00	Lunch and Coffee	14:10 Keynote	16:00 Closing ceremony
14:10	Keynote	14:40 Applications of Fuel Cell and Electrolyser Systems	
14:40	Low temperature fuel cells	15:40 Poster Session Coffee break	
15:40	Poster Session Coffee break	16:25 Keynote	
16:25	Polymer Electrolyte Fuel Cells and Electrolysers	16h55 Applications of Fuel Cell and Electrolyser Systems	
17:45		18:35	
		20h00 - 24h00	
		Gala dinner	

COMMITTEES

>> Local Organizing Committee (IMN, Nantes)

Olivier Joubert, Chairman

Guy Ouvrard

Annie Le Gal La Salle,

Eric Quarez,

Nathalie Barreau, Head

Richard Baschera

Isabelle Berthaud

Josselin Gesrel

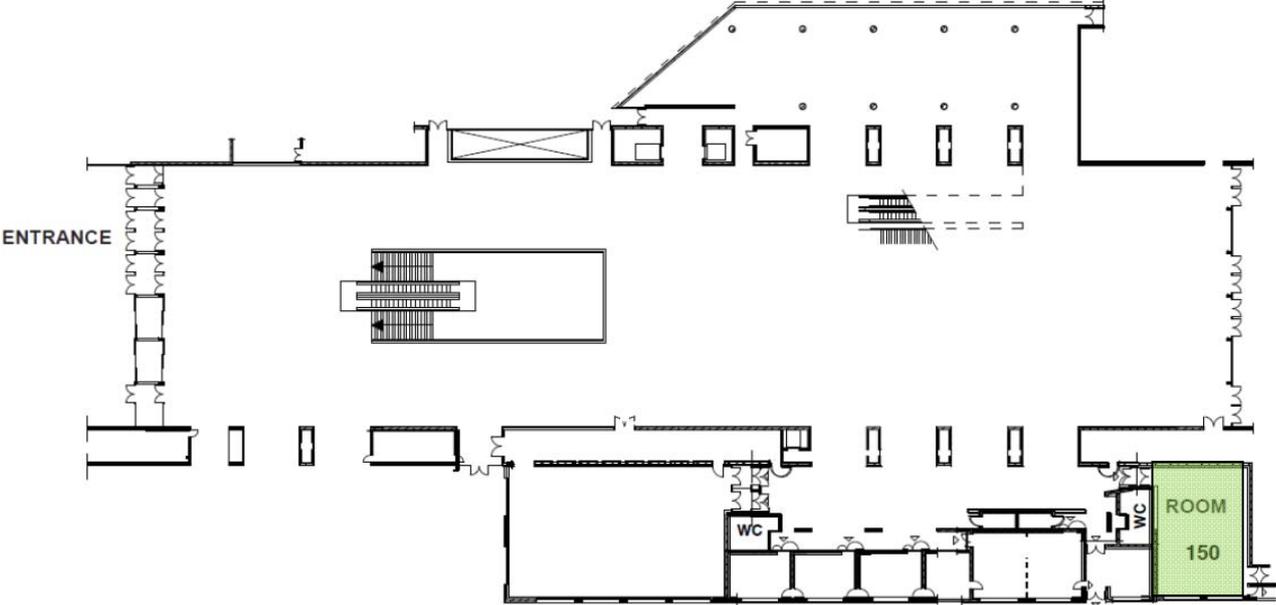
>> Special thanks to IMN Fuel Cells team students

>> International Advisory Committee

M.L. Fontaine (Norway), A. Brisse (Germany), J. Mougín (France), C. Turpin (France), M. Marrony (Germany), S.C. Singhal (USA), M. Dornheim (Germany), M. Latroche (France), T. Hashimoto (Japan), C. Coutanceau (France), A. Montone (Italy), Y. Filinchuk (Belgium), D. Hissel (France), G. Coors (USA), Didier Bouix (France), G. Pourcelly (France), F. Cuevas (France), K. Agbossou (Canada), J. Riera (Spain), P. Piccardo (Italy), M. Chatenet (France)

CONFERENCE CENTER MAP

Conference room : "ROOM 150"



DETAILED PROGRAM

8:00 - 19:00 Registration open

9:00 - 9:30: Opening Session

Conference Chair

Olivier JOUBERT (Director, HySPàC)

Director IMN: Guy OUVRARD

Major of the city Nantes: Véronique STEPHAN

Regional Council of the Pays de la Loire: Laurent GERAULT

9:30 - 10:15: Plenary

Chairman: Fermin CUEVAS

P1: Physisorption of hydrogen in highly porous compounds: state of the art and prospects.

Michel LATROCHE, ICMPE, Thiais, France

10:15 – 10:55: HYDROGEN PRODUCTION

Chairman: Fermin CUEVAS

10:15 – 10:35

O1: Oxidative biogas reforming for hydrogen production over cerium nickel and aluminum based catalysts

Yaqian WEI , UCCS, Lille, France

10:35 – 10:55

O2: Low temperature autothermal reforming of ethanol on nickel cerium based catalysyts for hydrogen production

Yann ROMANI, UCCS, Lille, France

10:55 - 11:25: Coffee Break

DETAILED PROGRAM

11:25 - 11:55: Keynote

Chairman: Michel LATROCHE

K1: Which materials for today's solid state hydrogen storage applications?
Dr. Fermin CUEVAS, ICMPE, Thiais, France

11:55 – 12:55: HYDROGEN STORAGE

Chairman: Michel LATROCHE

11:55 – 12:15

O3: Oscillatory mechanism of solid/gas interaction in the palladium/hydrogen system

Erwin LALIK, Jerzy Haber Institute of Catalysis and Surface Chemistry, Krakow, Poland

12:15 – 12:35

O4: Metal Hydrides for Hydrogen Storage: From Materials to Systems

Martin DORNHEIM, Helmholtz-Zentrum, Geesthacht, Germany

12:35 – 12:55

O5: Synthesis and cycling of MgH₂-TiH₂ nanomaterials for efficient solid gas hydrogen storage

Pavel RIZO, ICMPE, Thiais, France

13:00 - 14:10: Lunch

14:10 - 14:40: Keynote

Chairman: Sophie DIDIERJEAN

K2: Feedback of H₂ mobility demonstration projects led by EIFER and EDF in France
Dr. David COLOMAR, EIFER, Karlsruhe, Germany

14:40 – 15:40: LOW TEMPERATURE FUEL CELLS

Chairman: Sophie DIDIERJEAN

14:40 – 15:00

O6: Borohydride electro-oxidation at platinum electrodes: experimental and modeling insights

Marian CHATENET, LEPMI, Grenoble, France

15:00 – 15:20

O7: Electrochemical cells based on CsH₂PO₄ for operating at high pressures

Laura NAVARRETE, ITQ, Valencia, Spain

15:20 – 15:40

O8: Structure-transport interplay in highly phase separated aromatic block ionomers

Huu-Dat NGUYEN, LEPMI, Grenoble, France

DETAILED PROGRAM

15:40 - 16:25: Coffee Break/Poster Session

16:25 – 17:45: POLYMER ELECTROLYTE FUEL CELLS AND ELECTROLYSERS

Chairman: Marian CHATENET

16:25 – 16:45

O9: Kinetics of water sorption and desorption in NAFION® membrane: influence of the interfacial mass transfer coefficient

Sophie DIDIERJEAN , LEMTA, Nancy, France

16:45 – 17:05

O10: Microwave accelerated galvanic displacement of platinum on nickel nanofibers

Giorgio ERCOLANO, ICG-AIME, Montpellier, France

17:05 – 17:25

O11: Experimental investigation of performance degradation on an open cathode Proton Exchange Membrane Fuel Cell stored at sub-zero temperatures

Yi FANG, FCLAB, Belfort, France

17:25 – 17:45

O12: Towards ultrathin platinum films on nanofibers by surface limited electrodeposition for electrocatalytic applications

Filippo FARINA, ICG-AIME, Montpellier, France

DETAILED PROGRAM

8:00 - 19:00 Registration open

09:30 – 13:00: HIGH TEMPERATURE ELECTROLYSERS session
An ELECTRA EU project supported event.

9:30 - 10:00: Keynote

Chairman: Truls NORBY

K3: Segmented in series proton ceramic tubular electrolysis cells
Marie-Laure FONTAINE, SINTEF, Oslo Norway

10:00 – 10:40: SOLID OXIDE ELECTROLYSERS

Chairman: Marie-Laure FONTAINE

10:00 – 10:20

O13: Steam electrolysis using proton ceramic cells and modules - Design and performance modelling

Truls NORBY , University of Oslo, Oslo, Norway

10:35 – 10:55

O14: Anode performance based on high temperature proton conducting electrolyzers and a multitube module construction

Nuria BAUSA MARTINEZ, ITQ, Valencia, Spain

10:40 - 11:20: Coffee Break and Posters

11:20 – 13:00: SOLID OXIDE ELECTROLYSERS

Chairman: Jean-Claude GRENIER

11:20 – 11:40

O15: MANUFACTURING OF THIN FILM METAL SUPPORTED PCECs

Marie-Laure FONTAINE, SINTEF, Oslo Norway

11:40 – 12:00

O16: Performance and durability of Solid Oxide electrolyser stacks for hydrogen and syngas production

Olivier THOMANN, VTT Technical Research Centre, Finland

12:00 – 12:20

O17: OPTIMUM AMOUNT OF FUEL ELECTRODE POROSITY FOR AN INTERMEDIATE TEMPERATURE SOLID OXIDE ELECTROLYZER CELL

Dorna HEIDARI, School of Mechanical and aerospace Engineering, NTU, Singapore

12:20 – 12:40

O18: STEAM INJECTION FOR ELECTROLYSIS EXPERIMENTS AND HYDROGEN RECOVERY WITH SOFT MICA AS SEALING

Raphael IHRINGER, Fiaxell, Lausanne, Switzerland,

12:40 – 13:00

O19: STEAM ELECTROLYSIS USING PROTON CERAMIC CELLS

Einar VØLLESTAD , University of Oslo, Oslo, Norway

DETAILED PROGRAM

13:00 - 14:10: Lunch

14:10 - 14:40: Keynote

Chairman: Annie LE GAL LA SALLE

K4: Review of technologies for Marine Renewable Energies and Multi-Usage Offshore Platforms and opportunities for H₂ Storage.

Franck SCHOEFS, GEM-IUML, Nantes, France

14:40 – 15:40: APPLICATIONS OF FUEL CELL AND ELECTROLYSER SYSTEMS

Chairman: Franck SCHOEFS

14:40 – 15:00

O20: Using hydrogen storage to reach self sufficiency

Jean-Emmanuel BOUCHER, POWIDIAN, Chambray les Tours, France

15:00 – 15:20

O21: Preliminary design of a wind driven vessel dedicated to hydrogen production

Aurélien BABARIT, LHEEA Lab, Ecole Centrale Nantes, Nantes, France

15:20 – 15:40

O22: Applications of Energy Storage Systems for offshore wind production

Pierre WARLOP, wpd offshore France, Nantes, France

15:40 - 16:25: Coffee Break/Poster Session

DETAILED PROGRAM

16:25 - 16:55: Keynote

Chairman: Annie LE GAL LA SALLE

K5: Potentialities and challenges for introduction of fuel cell in aeronautical applications

Christophe TURPIN, LAPLACE, Toulouse, France

16:55 – 18:35: APPLICATIONS OF FUEL CELL AND ELECTROLYSER SYSTEMS

Chairman: Christophe TURPIN

16:55 – 17:15

O23: CONTRIBUTION OF OCV MEASUREMENTS DURING START-UP AND SHUT-DOWN PROCEDURES TO THE SOH ESTIMATION OF A H₂/O₂ PEM FC STACK: DEVELOPMENT OF ORIGINAL INDICATORS FOR THE INTERNAL H₂ LEAK ESTIMATION

Malik TOGNAN, LAPLACE, Toulouse, France

17:15 – 17:35

O24: ANODE SUPPORTED SOFC ON METALLIC FOILS

Paul GATEAU, SYNGAS, France

17:35 – 17:55

O25: Proton Exchange Membrane Fuel Cell Diagnosis by Spectral Characterization of the Electrochemical Noise

Radouane MAIZIA, Institut Pprime, Poitiers, France

17:55 – 18:15

O26: USING THE CHANNEL IMPEDANCE TO MEASURE AIR VELOCITIES IN POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

Stéphane CHEVALIER, LTN, Nantes, France

18:15 – 18:35

O27: FROM GAS PRODUCTION TO DIRECT ELECTRICITY PRODUCTION BY COUPLING OF A GASIFIER AND A NICKEL/YTTRIA-STABILIZED ZIRCONIA-BASED SOLID OXIDE FUEL CELL

Annie LE GAL LA SALLE, IMN, Nantes, France

20:00 - 24:00: Gala Dinner on The bateaux Nantais

The Gala Dinner is organized by the «Bateaux Nantais» (boats of Nantes). It is a dining cruise on the Erdre river. Meeting point : Quai de la Motte Rouge.

From La Cité-Nantes Events Centre, take the tramway line 1 (green) at «Duchesse Anne-Chateau des Ducs de Bretagne» stop, direction «François Mitterand» or «Jamet».

Get off at «Commerce» and commute to line 2 (red), direction «Orvault Grand Val». Get off at «Motte Rouge» stop.

Then, go upstairs and cross the bridge «Pont Général de la Motte Rouge». The boat station is the glass and green building on your left

DETAILED PROGRAM

8:00 - 18:00 Registration open

09:30 – 10:40: SOLID OXIDE FUEL CELL & ELECTROLYSERS

Chairman: Eric QUAREZ

09:30 – 09:50

O28: PROTON CERAMIC ELECTRODICS

Truls NORBY , University of Oslo, Oslo, Norway

09:50 – 10:10

O29: Optimization of the doped ceria as interlayer between the electrolyte and the SOFC oxygen electrode: electrochemical studies

Jean-Claude GRENIER, ICMCB, France

10:10 – 10:30

O30: ADVANCES IN THE UNDERSTANDING OF THE ENHANCED CONDUCTIVITY IN CARBONATE/OXIDE COMPOSITES AS ELECTROLYTE FOR SOLID OXIDE CELLS

Armelle RINGUEDÉ, IRCP, Paris, France

10:40 - 11:20: Coffee Break

11:20 – 13:00: SOLID OXIDE FUEL CELL & ELECTROLYSERS

Chairman: Armelle RINGUEDÉ

11:20 – 11:40

O31: Neutron diffraction as a characterization tool of SOFC materials under operating conditions

Mona BAHOUT, ISCR, Rennes, France

11:40 – 12:00

O32: Effect of doping level x in Ln_{1-x}MxCr_{0.9}Ni_{0.1}O₃ SOFC anodes

Aritza WAIN, Facultad de Ciencia y Tecnología, Leioa, Spain

12:00 – 12:20

O33: IMPEDANCE SPECTROSCOPY OF SOFC CATHODES : SOME EXAMPLES

Jean-Claude CARRU, ULCO UDSSM, Calais, France

12:20 – 12:40

O34: A novel efficient oxygen electrode for Solid Oxide Fuel Cells: Pr₆O₁₁

Clément NICOLLET, ICMCB, France

13:00 - 14:00: Lunch

DETAILED PROGRAM

14:00 – 16:00: MATERIALS FOR HYDROGEN STORAGE AND TRANSFORMATION

Chairman: Fermin CUEVAS

14:00 – 14:20

O35: Synthesis and properties of doped $Ba_3Ti_3O_6(BO_3)_2$: a new SOFC electrolyte?

Jean-Marie DOUX, IMN, Nantes, France

14:20 – 14:40

O36: Deposition of ceria barrier layer by d.c. magnetron sputtering under reactive conditions

Pierre CODDET, GREMI, Orléans, France

14:40 – 15:00

O37: Synthesis and corrosion mechanisms of $Y_{2-x}Mg_xNi_7$ intermetallics during soaking in alkaline medium for use as negative electrode in Ni-MH batteries

Nicolas MADERN, ICMPE, Thiais, France

15:00 – 15:20

O38: New borane-amide based materials as potential solid state hydrogen storage materials

Salem OULD-AMARA, IEMM, Montpellier, France

15:20 – 15:40

O39: Hydrogen interaction with Pd-Ir nanoalloys supported on carbon: composition and size effect

Abdelmalek MALOUCHE, ICMPE, Thiais, France

15:40 – 16:00

O40: Experimental and modeling investigations on hydriding phenomena based on various charging scenarios

Dimitri CLAUDEL, FEMTO ST, Besançon, France

16:00 - 16:10: Closing ceremony

PO1: SIMULATION OF MECHANICAL STRENGTH OF HYDROGEN WOUND COMPOSITE PRESSURE VESSELS SUBJECTED TO FIRE

Damien HALM, Institut Pprime, Poitiers, France

PO2: EXPERIMENTAL INVESTIGATION ON WATER TRANSFER IN PASSIVE TYPE PEFC MODULE

Eiji Ejiri, HIBA Institute of Technology, Narashino, Japan

PO3: MODELLING AND SIMULATION OF THE 46 KW PEM HIGH PRESSURE WATER ELECTROLYZER INSTALLED ON THE MYRTE PLATFORM

Manuel ESPINOSA, University of Corsica, Ajaccio, France

PO4: Understanding ternary PEMFC nanocatalyst atomic arrangement during growth and annealing: a Molecular Dynamics approach

Pascal BRAULT, GREMI, Orléans, France

PO5: Characterization and modeling of commercially available High Temperature PBI-H₃PO₄ based MEAs in various operating conditions

Sylvain RIGAL, IRT St Exupéry, Toulouse, France

PO6: SAMARIA-DOPED CERIA/(Li,Na,K)CO₃ COMPOSITE AS POTENTIAL ELECTROLYTES IN HYBRID FUEL CELL (350-450°C)

Armelle RINGUEDÉ, IRCP, Paris, France

PO7: RESEARCH OF NEW ELECTROLYTE MATERIALS FOR SOLID OXIDE FUEL CELLS

Jean-Marie DOUX, IMN, Nantes

ABSTRACTS

Plenary P1:

Physisorption of hydrogen in highly porous compounds: state of the art and prospects.

Michel Latroche

Institut de Chimie et des Matériaux Paris Est, CNRS UPEC, 2 rue H. Dunant, 94320 Thiais, France

Email: michel.latroche@icmpe.cnrs.fr, web site: <http://www.icmpe.cnrs.fr>

Combining targeted chemistry, computational design, and innovative synthesis processes, a large variety of porous materials can be obtained with very large pore sizes and giant surface areas. Besides the usual applications of such porous compounds, it has been shown that they exhibit potential properties for hydrogen gas physisorption. Such compounds can be used for the storage of H₂. Interestingly, they exhibit low enthalpies, weak activation energies and fast kinetics. The sorption properties of various materials, covering carbon and metal-organic frameworks (MOFs), will be presented and compared, regarding volumetric and gravimetric uptake as a function of the textural properties.

KEYNOTE K1:

WHICH MATERIALS FOR TODAY'S SOLID STATE HYDROGEN STORAGE APPLICATIONS?

Fermin Cuevas, Michel Latroche

ICMPE, Université Paris Est, CNRS, UPEC, UMR7182, F-94320 Thiais, France

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Aiming to mitigate the issues of climate change and economic dependence on fossil fuels, hydrogen is considered as an ideal energy carrier for both mobile and stationary applications. Its low volumetric density is however a serious drawback for its storage. Three main techniques exist to store hydrogen [1] *i*) gas storage at high hydrogen pressures (700 bar) in composite tanks, *ii*) liquid storage at low cryogenic temperatures (21 K) using insulated tanks and *iii*) solid-state storage under hydrogen pressures and temperatures close to ambient conditions, which ultimately improves storage efficiency and safety.

After several decades of research in solid state hydrogen storage, many hydrogen-containing compounds (metal and intermetallic hydrides, alanates, borohydrides, imides/amides...) have been discovered and their fundamental hydrogenation properties (thermodynamics, capacity, kinetics, cycle-life...) determined [2]. Quite often, their ability to store hydrogen is given considering their gravimetric and volumetric capacities as the main criteria. Although these parameters are intrinsic fundamental ones, the first criterion for a given application is the reversibility of the hydrogen uptake/release reaction under the pressure and temperature conditions of operation. Such reversibility is proved and usually characterized by monitoring pressure-composition-temperature isotherms. Following these considerations, main materials used today in solid-state hydrogen storage tanks are limited to intermetallic hydrides and few complex hydrides [3]. All these concepts will be reviewed and supported by examples of compounds used in prototypes and practical applications.

References:

- [1] J.-M. Joubert, F. Cuevas, M. Latroche, A. Percheron-Guégan, *Ann. Chim.-Sci. Mat*, 30 (2005) 441-454
- [2] Q. Lai, M. Paskevicius, D. A. Sheppard, C. E. Buckley, A. W. Thornton, M. R. Hill, Q. Gu, J. Mao, Z. Huang, H. K. Liu, Z. Guo, A. Banerjee, S. Chakraborty, R. Ahuja and K.-F. Aguey-Zinsou, *ChemSusChem*, 8 (2015) 2789-2825
- [3] M. Ley, M. Meggouh, R. Moury, K. Peinecke, M. Felderhoff, *Materials* 8 (2015) 5891-5921.

**KEYNOTE K2:
FEEDBACK OF H2 MOBILITY DEMONSTRATION PROJECTS LED
BY EIFER AND EDF IN FRANCE**

David Colomar^a, Henri-Bruno Calmels^b, Volker Schlabach^a, Annabelle Brisse^a

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Hydrogen and fuel cells represent one solution for low-carbon mobility, provided hydrogen is produced with non-fossil energy sources, such as carbon free electricity. In this context, electrolysis can play an important role. However there are still several challenges to be met, from the improvement of core technologies in electrolysis and hydrogen refueling stations, to the development of innovative business models.

EIFER and the EDF group have been actively working in the development of innovative solutions for low-carbon hydrogen mobility through the development and tests of breakthrough technologies for hydrogen refueling stations and the participation to demonstration projects. This abstract presents the status and current results of 4 emblematic demonstration projects in which EIFER and EDF are involved in France.

The projects are presented. The technical concepts of the demonstrators are described, as well as the targeted business cases. The experience gained during the preparation phase of the projects is explained, including administrative and technical issues. The problematics related to the construction phase are also highlighted. For the projects where stations are already in operation, results of the demonstration phase are presented.

One of the main results of the ongoing projects at EIFER and EDF is that further research is required on some major components, despite most of the technologies are supposed to be mature: there are still major challenges on cost reductions that might be only achieved through the development of strongly innovative solutions. The point of view of EIFER and EDF on the need for further research is described.

The role that a major utility can play in this context is discussed.

KEYNOTE K3:
**SEGMENTED-IN-SERIES PROTON CERAMIC TUBULAR
ELECTROLYSIS CELLS**

Marie-Laure Fontaine^a, Dustin R. Beeff^b, Ragnar Strandbakke^c, E. Vøllestad^c, Christelle Denonville^a, Wen Xing^a, Zuoan Li^a, J.M. Serra^d, Truls Norby^c, Partow P. Henriksen, Rune Bredesen^a

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Incentives for developing high temperature electrolyzers (HTEs) using proton conducting electrolytes stem from the fact that a proton ceramic electrolysis cell (PCE) pumps out and pressurises dry H₂ directly. It is also anticipated that delamination of electrodes due to O₂ bubbles in solid oxide electrolysis cells (SOEs) will be alleviated in PCEs. Existing HTEs design utilises the high packing density of planar stacks, but the hot seal and vulnerability to single cell breakdown give high stack rejection rate and questionable durability and lifetime economy. We investigate instead tubular cells, mounted in a novel module with cold seals that allows monitoring and replacement of individual tubes from the cold side. Innovative tubular segmented-in-series cells are developed along three main lines with increasing risks/rewards. All cells consist of a porous Ni-BZCY cathode for the H₂ side (self-standing or supported on a porous BZCY tube), a dense BZCY-based electrolyte, a porous anode for the H₂O+O₂ side, and a current collector system. The 1st line is based on solid state reactive co-sintering of BZCY based electrolyte coated on a slip-cast or extruded NiO based composite tube. Various cell architectures of 25 cm tube length were produced with varying Ce contents and are used for investigation of anode and current collection system. In the 2nd line, the BZCY tubes are cut and stacked in series to build voltage and reduce overall current to improve current collection along the tube. This path is suitable for reaching good module performance, although mass scale production may not be the most efficient. These cells are currently tested. The 3rd line takes a closed porous BZCY based extruded tube, on which segments of cathode (NiO-BZCY), BZCY electrolyte, and interconnect are sequentially applied and sintered. This path is suitable both for reaching good module performance and efficient mass scale production. Tailoring of cell architectures, in particular of Ce content and of NiO sintering aid is decisive to avoid differential shrinkage between the delineate bands, as well as to avoid delamination and obtain dense electrolyte. Three interconnect systems are currently screened based on (La,Sr)(Mn,Cr)O₃, TiNb₂O₇-BGLC, and metal-glass composites. The air electrode consists of the double perovskite Ba_{1-x}Gd_{0.8}La_{0.2+x}Co₂O_{6-δ} (BGLC). BGLC (x = 0.3) has been tested as oxygen/steam electrode on segments. A total area specific polarization resistance of 1 Ω.cm² is obtained at 600 °C in 5 % H₂ in Ar / 2.5 % H₂O in 1 atm O₂. Complete cells with BGLC electrodes are currently tested in electrolysis mode. Results of this work will be presented highlighting progress and challenges in cells manufacturing and performance.

Acknowledgements: The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621244.

KEYNOTE K4:
**Review of technologies for Marine Renewable Energies and Multi-Usage
Offshore Platforms and opportunities for H2 Storage**

Franck SCHOEFS

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**KEYNOTE K5:
Potentialities and challenges for introduction of fuel cell in aeronautical
applications**

Christophe TURPIN

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OXIDATIVE BIOGAS REFORMING FOR HYDROGEN PRODUCTION OVER CERIUM NICKEL AND ALUMINUM BASED CATALYSTS

Yaqian Wei^a, Cyril Pirez^a, Sébastien Paul^a, Louise Jalowiecki-Duhamel^{a,*}

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With the continually growth of the exploitation and utilization of fossil fuels as well as the excessive greenhouse gas (GHG) emissions worldwide, developing hydrogen as a promising future energy has drawn significant interest [1,2]. In order to support a clean and sustainable hydrogen economy, it is urgently desirable to produce hydrogen from renewable energy sources, such as biomass-derived materials and/or biogas [3]. Biogas, a mixture of gases mainly containing methane (CH₄) and carbon dioxide (CO₂), which is a result of the anaerobic digestion of various bio-resources, appears as being clean and renewable for reforming process. This study focuses on the low temperature oxidative simulated biogas reforming, which is a combination of dry reforming and partial oxidation reforming of methane.

CeNi_xAl_{0.5}O_y ternary mixed oxides were synthesized by the co-precipitation method and subsequently characterized by elemental analysis, XRD, H₂-TPR, and Raman techniques. The catalytic activity of the catalysts with different Ni content was studied in the reaction of oxidative biogas reforming and compared to the classical dry reforming. As an example, the effect of nickel content is shown in Figure 1. CeNi_xAl_{0.5}O_y catalysts are shown highly efficient for H₂ production at low temperature (500-600°C), with results quite close to the predicted equilibrium values. The addition of O₂ increases the H₂ production significantly at low temperature, allowing H₂/CO ratio to be raised slightly. However, excessive O₂ feeding reduces the CO₂ conversion efficiency. The influence of different parameters has been studied in order to find optimal conditions. Moreover, carbon formation is carefully measured after test and it is strongly related to the Ni content and presence of Al. The oxidative simulated biogas reforming exhibits high conversions and selectivity on the studied catalysts, demonstrating that combination of DRM and POM can be performed efficiently.

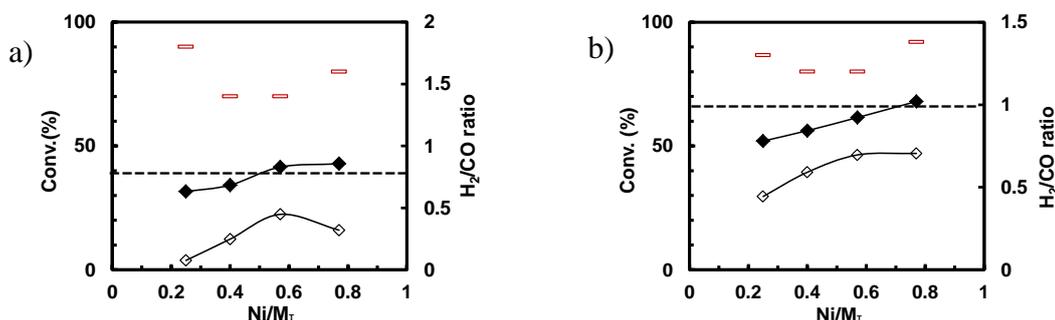


Figure 1: CH₄ (◆) and CO₂ (◇) conversions and H₂/CO ratio (□) versus Ni content over CeNi_xAl_{0.5}O_y catalysts at (a) 500°C and (b) 600°C. (CH₄ conversion thermodynamic limit ---, reaction conditions : CH₄/CO₂/O₂/N₂=1:0.7:0.3:N₂. M_T is total metal: Ni+Ce+Al).

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LOW TEMPERATURE AUTOTHERMAL REFORMING OF ETHANOL ON NICKEL CERIUM BASED CATALYSTS FOR HYDROGEN PRODUCTION

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Nowadays, hydrogen is mainly produced from fossil resources at high temperature. With the objective to use a “greener” energy, it is mandatory to use reactants issued from biomass and to develop catalysts performing at low temperature to save energy and limit pollution. Oxidative steam reforming (OSR) that combines partial oxidation and steam reforming allows using low energy input. In the laboratory, cerium nickel based oxyhydride catalysts ($\text{CeNi}_x\text{H}_z\text{O}_y$), have been reported for low temperature hydrogen production from ethanol in presence of water and oxygen in specific conditions [1-3]. In the present study, the performance of such catalysts has been studied in autothermal reforming (ATR) conditions which requires specific oxygen and water concentrations ($\text{CH}_3\text{CH}_2\text{OH} + 0.6 \text{O}_2 + 1.8 \text{H}_2\text{O} \rightarrow 4.8 \text{H}_2 + 2 \text{CO}_2$). As an example, Figure 1 shows that stable conversions are obtained at 300°C on the $\text{CeNi}_1\text{H}_z\text{O}_y$ nano-oxyhydride catalyst. The main products of the reaction are H_2 (~40%), CO_2 (~30%), CH_4 (~20%) and CO (~10%) with a small quantity of other products (< 1%). Therefore, very interesting results are obtained using a non-noble metal catalyst at low temperature and involving a low mass of catalyst [4,5]. The influence of different parameters has been studied and different physicochemical characterizations (XRD, Raman, ICP, etc.) have been done in order to obtain correlations between catalytic activity and solid properties, and will allow a discussion on active site and mechanism.

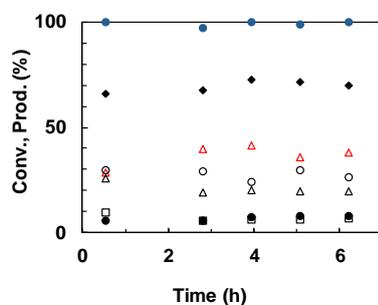


Figure 1 : Ethanol (◆) and oxygen (●) conversions and products distribution (H_2 (△), CO_2 (○), CO (●), CH_4 (△) and CH_3CHO (□)) obtained at 300°C on the $\text{CeNi}_1\text{H}_z\text{O}_y$ nano-oxyhydride catalyst. (Catalyst: 50 mg. Reaction conditions: $\text{H}_2\text{O}/\text{EtOH}/\text{O}_2/\text{N}_2 = 1.9/1/0.6/\text{N}_2$)

Y. Romani thanks for a grant from “Ecole Centrale de Lille” and “Région Hauts-de-France”.

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OSCILLATORY MECHANISM OF SOLID/GAS INTERACTION IN THE PALLADIUM/HYDROGEN SYSTEM

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Metallic palladium has a unique property of being able to absorb large amounts of gaseous hydrogen into its crystal lattice, and it is well established that the hydrogen is accommodated within the Pd lattice in the atomic form. Hence, the dissociation of molecular hydrogen and the formation of atomic hydrogen species must occur on the Pd surface prior to their penetration into the Pd bulk. However, the actual chemical mechanism of the process is not sufficiently understood. Here we propose a novel mechanism of the hydrogen sorption in Pd consisting of two temporally separated sub-processes: The first sub-process (1) consists merely of adsorption of molecular hydrogen H_2 on the Pd surface without its dissociation. The second sub-process (2) sees the adsorbed H_2 dissociated and the hydrogen atomic species so formed penetrating into the lattice of Pd. Crucially, the sub-process (2) only begins when a certain critical coverage of molecular hydrogen is being reached on the surface of Pd, providing for the temporal separation of the two sub-processes and making it possible for them to proceed alternately. The two sub-processes also differ greatly in their respective thermal effects, with the sub-process (2) being much more energetic of the two. Thus, the heat during the sorption may as well evolve in the alternating manner, and indeed, the thermokinetic oscillations have been reported for this process [1-3], measured using gas flow-through microcalorimetry. Combining (to our best knowledge for the first time) the latter method with the potentiostatic measurements in situ of a low-voltage current flowing in the palladium powder exposed to hydrogen(deuterium) made it possible to reveal a strict correlation between the frequency of thermokinetic oscillations ($P(t)$ in Figure 1) and the periodicity of the time series representing the first derivative of the current in time (dI/dt in Figure 1). Rationalization of this unexpected correlation has provided a base for the formulation of the novel mechanism described above.

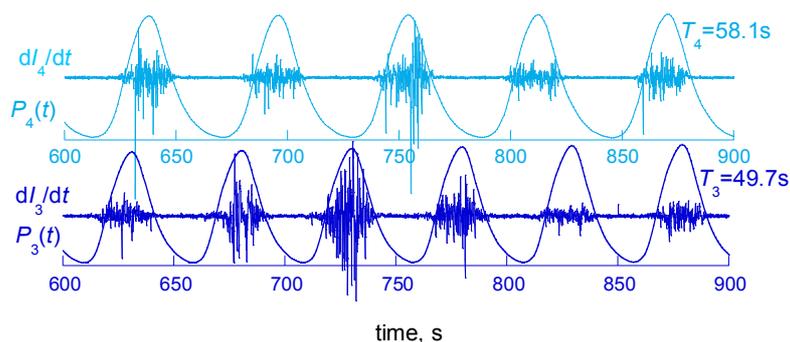


Figure 1. Examples of the correlation between the oscillatory heat evolution $P(t)$ in the sorption of deuterium in Pd powder and the first derivative of low-voltage current dI/dt flowing through the Pd powdered sample during the process for two different oscillation periods T .

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ORAL O4
Metal Hydrides for Hydrogen Storage: From Materials to Systems

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ORAL O5:
**SYNTHESIS AND CYCLING OF MgH₂-TiH₂ NANOMATERIALS FOR
EFFICIENT SOLID-GAS HYDROGEN STORAGE**

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MgH₂ is an outstanding hydrogen store but is too stable for room temperature applications and suffers from poor kinetics. The latter drawback is attributed to low catalytic activity of Mg toward H₂ dissociation and slow hydrogen diffusion in the hydride phase. Nanostructuring and dopant addition, such as TiH₂ [1,2], allows to alleviate this issue. This work aims to determine the effect of the TiH₂-amount on the reversible hydrogen capacity of the (1-y)MgH₂-yTiH₂ system. Nanocomposites with different TiH₂-contents (y = 0, 0.05, 0.1, 0.2 and 0.3) were synthesized by reactive ball milling. The crystal structure was characterized by powder X-ray Diffraction (XRD). Kinetic and cycling hydrogenation properties have been analysed using a manometric Sievert's type apparatus. For each nanocomposite, twenty H-sorption cycles at 300 °C were performed. Quasi-static absorption and desorption pressures of 0.8 and 0.03 MPa were used, respectively. Reaction time was limited to 15 min.

As the main outcome of this study, we conclude that it exists an optimum value for the TiH₂ content. This is illustrated in Fig. 1 where the reversible storage capacity of the nanocomposites as a function of TiH₂ amount is displayed. After 20 sorption cycles (continuous line), the reversible capacity passes through a maximum (5.3 wt.% H) at y = 0.1. This maximum can be explained by the crossover between the nominal capacity of the composites (black dashed line) and the capacity retention upon cycling (red dashed line). For low TiH₂ contents (y < 0.1), the capacity retention is poor due to the slowing down of sorption kinetics related to severe crystal growth. At higher contents (y > 0.1), the nominal capacity of the composites (dashed line) decreases due to the dead-weight of the TiH₂ phase as this hydride is too stable at the studied cycling conditions.

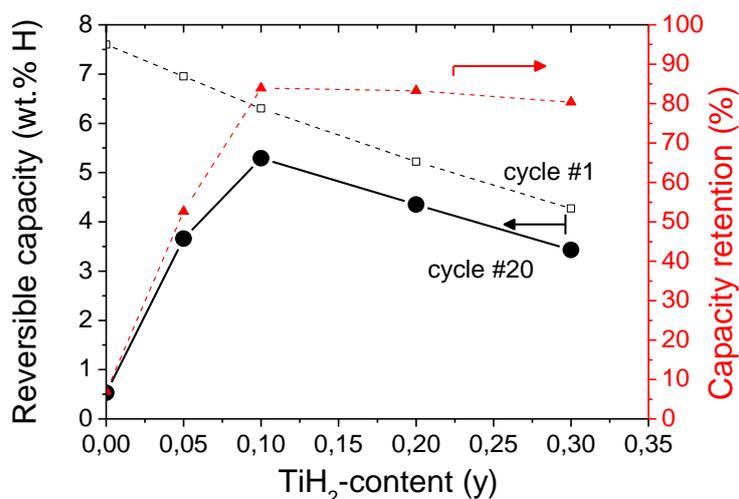


Fig 1. Reversible hydrogen storage capacity of yMgH₂-(1-y)TiH₂ nanocomposites.

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BOROXYDRIDE ELECTROOXIDATION AT PLATINUM ELECTRODES: EXPERIMENTAL AND MODELLING INSIGHTS

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The electrooxidation of BH_4^- (BOR) is a complex reaction and competes with its heterogeneous hydrolysis on most catalytic surfaces (1). Gold and platinum are the most studied electrocatalysts for the BOR (2), but despite intense efforts, the reaction mechanisms at such electrodes are still unclear. In this contribution, the BOR was studied using several Pt-based model electrodes (bulk Pt and Pt nanoparticles supported on various carbon substrates). It was demonstrated that the BOR is largely influenced by the morphology of the Pt surface, putting forward the complex mechanism of the reaction and in particular clear effects of the residence time of reaction intermediates on its overall completion and even nature. Hydroxyl species formation (for $E > 0.6$ V vs. RHE) on the Pt surface play a pivotal role on the reaction: they enable the removal of the BH_x adsorbed intermediates (that block the Pt surface at low potential) in a Langmuir-Hinshelwood type electrooxidation (Figure 1A), but this proceeds at the detriment of the fraction of free Pt sites and affects the BOR pathway. The dual role of the OH_{ad} species, but also, the generation of H_2 from the catalytic decomposition of BH_4^- and/or electroreduction of water followed by its electrooxidation or escape, were modelled based on experimental and calculated findings of the literature (Figures 1B) (3).

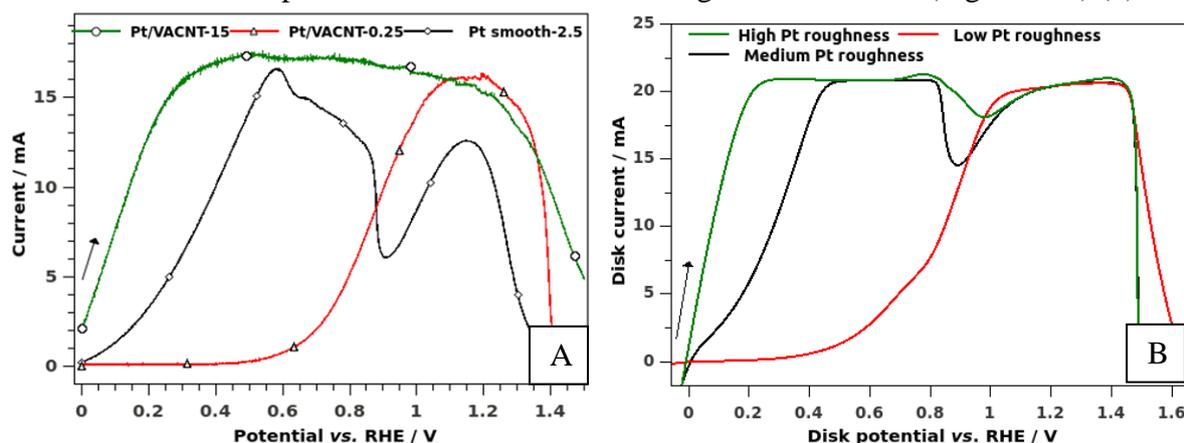


Figure 1: (A) experimental and (B) modelled BOR CV in quasi-stationary conditions (10 mM NaBH_4 in 1 M NaOH at 25 mV s^{-1} , 2500 rpm) obtained at Pt/Vertically Aligned Carbon NanoTube (VACNT) electrodes of various Pt loading (corresponding to various Pt roughness).

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ORAL O7:

Electrochemical cells based on CsH₂PO₄ for operating at high pressures

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CsH₂PO₄ has become as one of the new generation electrolytes for fuel cells operating at intermediate temperature (200 - 300 °C) [1]. CsH₂PO₄ transforms into cubic phase showing superprotonic conductivity when the temperature is increased above 230 °C [2]. Unlike the high temperature cells, the low operation temperature of CsH₂PO₄ allows cheap materials for the stack construction to be used and thus reducing the cost of the device. Moreover, due to the higher operation temperature, compared with polymeric membrane fuel cells (80 °C), different catalysts instead of platinum can be employed.

Usually, the same material can be used as electrolyte in a fuel cell or electrolyser cell, but the reactions involved are reversed. This premise was taken into account and CsH₂PO₄ was tested as electrolyte material in a fuel cell and electrolyser mode.

Different configurations of the cell have been studied to optimize its performance. Firstly, symmetrical cells supported on the electrolyte were manufactured by employing the same electrode material for cathode and anode. Carbon Gas Diffusion Layer (GDL) was employed as electrode and different catalysts as Cu, Zn and Pt were introduced by submerging the carbon paper into precursor solutions. Secondly, the electrolyte thickness was reduced by supporting the cell on different supports: steel or nickel porous supports. The electrolyte could be reduced from 1.8 mm to 100 µm. Further studies were performed in order to improve the mechanical stability of the sample. The addition of an epoxy in the electrolyte [3] allowed working with system pressure of 20 bar. Different ratios of CsH₂PO₄ and epoxy were studied in order to obtain good conductivity and good mechanical stability.

Concerning electrodes, some improvements were performed as to enlarge the triple phase boundary. A composite electrode with protonic and electronic conductivity was designed. CsH₂PO₄ and carbon powder impregnated with different metals were mixed manually.

Electrochemical Impedance Spectroscopy technique was used for the cell components characterization. The electrolyte conductivity was very influenced by the temperature but no significantly changes were obtained above 240 °C (0.015 S·cm² at 240 °C and 0.037 S·cm² at 250 °C). However, the electrode performance was highly influenced by temperature.

Furthermore, the influence of total pressure was tested for the different cells, and the results showed that changing from atmospheric to 4.5 bar of absolute pressure, the performance increased in more than six times. The results highlight the big influence of the system pressure in the cell performance. During the electrolysis, the composition of the outlet stream was monitored by a mass spectrometer and a chromatograph, in order to check the Faraday's efficiency.

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STRUCTURE-TRANSPORT INTERPLAY IN HIGHLY PHASE-SEPARATED AROMATIC BLOCK IONOMERS

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The relation between chemical architecture, microstructure and proton transport efficiency of a promising alternative to Nafion[®], i.e., ionomers based on multiblock copoly(arylene ether sulfone)s bearing perfluorosulfonic acids^{1,2} were systematically investigated by SANS analysis in different physical states, i.e., dry/hydrated polymer films, and diluted polymer solution. The SANS spectra of hydrated membranes showed two defined scattering maxima, ascribed to the well-organization at two different length scales (d_{ionic} , d_{block}). The alternated segmentation of hydrophobic (FPES) and hydrophilic (ps-PES) blocks, along with the phase separation between polar side chains (ps-) and non-polar PES backbone, lead to a complex multi-scale three-phase structure. This structure derives from packing rod-like elongated polymer particles in solution during solvent evaporation (**Fig. 1**). The swelling laws, i.e., the expansion of ionic domains (Δd_{ionic}) and block structure (Δd_{block}), were obtained by analyzing the peak evolution upon hydration number (λ). The presence of perfluorinated ionic side chains induces neat phase-separation and 1D-to-2D morphological evolution along λ . The transport properties were further analyzed using the microscopic structural sizes (d , Δd) as the relevant variables. The proton conductivity and the self-diffusion coefficient of water were found to vary linearly with confinement (Δd_{ionic}) and connectivity (block superstructure), although they have a differently balanced impact depending on the hydration regime (low vs high). With this work, we are now in the position to optimize the development of alternative PEMs by tailoring the materials in terms of IEC, side-chain, and block design, towards the best architecture-structure-transport interplay for high PEMFC-oriented performances.

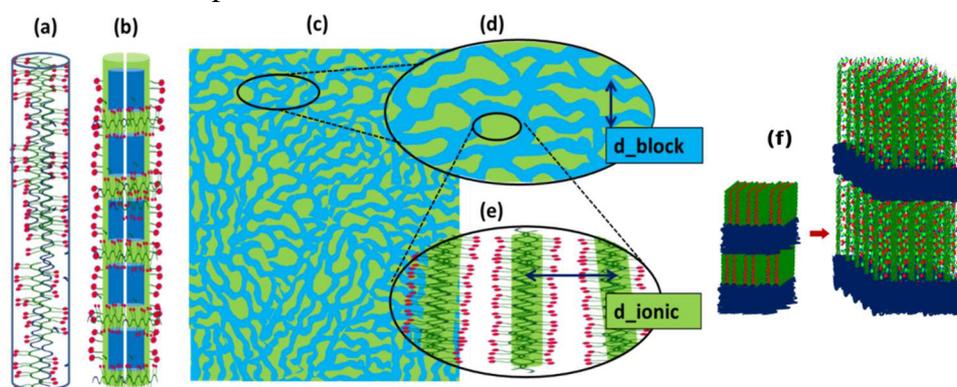


Figure 1. Schematic representation of the block copolymer structure.

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KINETICS OF WATER SORPTION AND DESORPTION IN NAFION[®] MEMBRANE: INFLUENCE OF THE INTERFACIAL MASS TRANSFER COEFFICIENT

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Keywords: Membrane, Water transport, Sorption, Desorption

Water sorption and desorption in Nafion[®] 117 membrane in acid form were studied by means of dynamic experiments as a response of relative humidity steps from 20% to 80% using a balance IGASORP (Hiden Isochema Ltd) which allows measuring very small mass variations with an accuracy of about 1 μg . The recorded mass variations with time of the membrane samples were analyzed by means of the least squares method based on a model taking into account a transfer resistance at the interface between the membrane and the surrounding humid gas [1]. As the diffusion time is small (the diffusion coefficient being large), the diffusive internal resistance can be neglected compared to the interfacial resistance so that the water content of the membrane can be assumed uniform, which was confirmed using NMR [2]. The model allows to show that the kinetic of the desorption is faster than for the sorption, and the comparisons with the experimental results show good accordance and give the value of the corresponding mass transfer coefficients (figure 1).

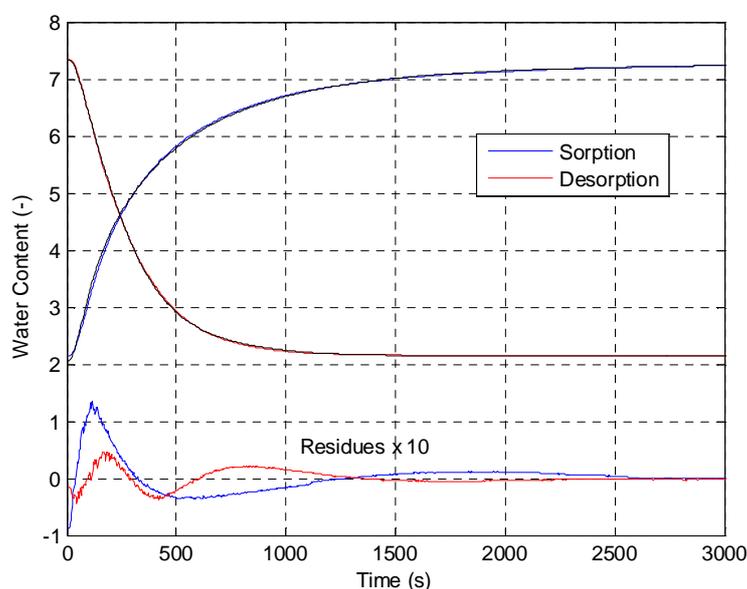


Figure 1. Mass variations (experimental results in blue and red) in response to HR variation between 20% and 80% for $T = 25^{\circ}\text{C}$. The corresponding calculated results are given in black, and the residues are magnified by 10.

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MICROWAVE ACCELERATED GALVANIC DISPLACEMENT OF PLATINUM ON NICKEL NANOFIBRES

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Pt/Ni based electrocatalysts for Proton Exchange Membrane Fuel Cell (PEMFC) have attracted the interest of several research groups and have been demonstrated capable of high platinum exploitation. Currently Pt/Ni alloy¹ and de-alloyed² nanoparticles are some of the few to have met the 0.44 A/mg_{Pt} 2020 DOE target for the oxygen reduction reaction (ORR) mass activity at 0.9 V_{RHE}³ for automotive applications. Using the same metallic system 3M reported nanostructured thin film catalyst based on de-alloyed Pt/Ni films supported on whiskers with mass activity values in the range 0.35-0.59 A/mg_{Pt}⁴. The nature of the extraordinary activity shown by the Ni/Pt system (mass activity in the range 0.6-1.6 A/mg_{Pt}) is attributed to a delicate balance a thin Pt shell and the subsurface Ni content¹.

A possible easy approach to a mass production of Ni/Pt electrocatalysts is the galvanic displacement of Ni nanofibres⁵. This Pt/Ni core/shell fibres have shown mass activity up to 1 A/mg_{Pt}. We demonstrate that is possible to reduce the reaction time required by the Pt-Ni galvanic displacement using a microwave-assisted procedure on Ni nanofibres. The obtained fibres have similar properties to those produced with conventional reactions. The microwave-assisted galvanic displacement is capable of producing high mass activity catalysts (0.4 A/mg_{Pt}) in just a fraction of the time required by the previously reported methods: the reaction time was reduced 200 fold (from 5-6 hours to 2 minutes)⁶. Furthermore, by tuning the Pt content it was possible to produce Pt/Ni core/shell catalysts that do not require electrochemical etching of surface Ni or de-alloying before utilisation making them a safer choice for PEMFC applications.

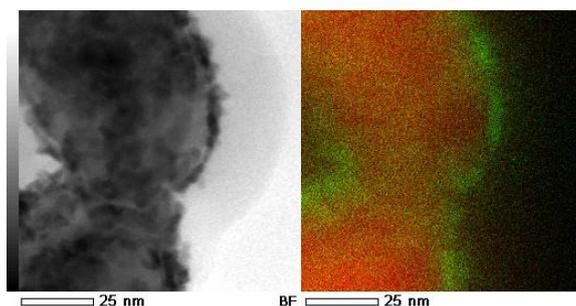


Figure 1 Bright Field STEM image of a Pt/Ni core/shell nanofiber and correspondent EDX elemental map (Pt in green, Ni in red)

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ORAL O11:

Experimental investigation of performance degradation on an open cathode Proton Exchange Membrane Fuel Cell stored at sub-zero temperatures

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The Proton Exchange Membrane Fuel Cell (PEMFC) is one of the most developed fuel cell technology in recent years [1] while the durability of PEMFCs still remains as a main factor that restricts their commercialization at a larger scale [2]. This issue becomes even more challenging under difficult operational conditions, especially in regions with extreme cold winter or wet tropical climate. For example, a potential application of PEM fuel cell in cold regions is to power a high-altitude mountain refuge, where the connexion to the grid is impossible. Coupled with a solar panel and an electrolyzer, the fuel cell can fulfill the power need of the visitors.

As the fuel cell will often be at its resting state during severe winter when there is no visitors in the refuge, the experimental research on the degradation of PEM fuel cell under this condition is necessary. Furthermore, prognostic tools are also needed to predict the state of health and to estimate the Remaining Useful Lifetime (RUL) of fuel cells, in order to make the systems more reliable, and to maintain them more efficiently with reduced costs. The aim of this work is to present the first experimental results of an open cathode PEM fuel cell gone through negative temperatures.

As a certain number of researches [3-5] have shown evident performance losses of PEM fuel cells after suffering freezing-thaw cycles, some studies investigated the mechanisms of degradation within the PEM fuel cells structures at micro scale ($\sim\mu\text{m}$). Scanning Electron Microscope images show material damages at different locations of PEMFCs, especially at gas diffusion layer, catalyst layer and membrane levels. The principal cause of these damages are due to the remaining water produced by chemical reactions within the fuel cell. During the freezing state, the formation of ice from water could lead to irreversible degradations and reduce largely the remaining useful lifetime of PEM fuel cells.

In this work, a test bench has been designed in lab to characterize two identical open

cathode PEMFCs, by performing polarization curve and Electrochemical Impedance Spectroscopy (EIS) of the fuel cells. After the first characterization, one of the fuel cell will undergo negative temperature cycles as low as -30°C for 20-day-long duration in a cold-room, and then will be characterized again in order to be compared to the other fuel cell which will be stored under normal environmental conditions.

With this comparison study, the influence of extreme negative temperatures on the performance of a typical open cathode PEM fuel cell will be observed, and raw experimental data for later prognosis will be gathered in order to predict the RUL.

As a perspective, an algorithm of prognosis based on Reservoir Computing (RC), which is a new paradigm of artificial neural networks will be tested with the experimental data.

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TOWARDS ULTRATHIN PLATINUM FILMS ON NANOFIBRES BY SURFACE-LIMITED ELECTRODEPOSITION FOR ELECTROCATALYTIC APPLICATIONS

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Conventional cathode electrocatalysts for Proton Exchange Membrane Fuel Cells (PEMFCs) are based on Pt nanoparticles supported on high surface carbon powders; in recent years, 1D nanomaterials have shown promising characteristics for the replacement of this conventional support due to their high aspect ratio, porosity and structure^[1]. Among various techniques, electrospinning is an attractive method to produce nanofibrous mats with fine control on porosity and fibres diameter, also providing the possibility of scale-up^[2]. On the other hand, the reduction of Pt catalyst loading is nowadays one of the greatest challenges for PEMFC development. The formation of extended surfaces has been recognized as a powerful strategy to maximize Pt utilisation and mitigating support corrosion in fuel cell operating conditions^[3].

Pt film formation is therefore a key aspect of the electrocatalyst preparation. State-of-the-art electrodeposition methods are capable of producing nanoparticles in the range 50-200 nm^[4]. In this work, we describe a novel high overpotential surface-limited deposition method^[5]; by varying the electrodeposition parameters we demonstrate that it is possible to produce Pt ultrathin films, nano-platelets and nanoparticles on different substrates, from model surfaces (glassy carbon and HOPG) to electrospun carbon nanofibres (Figure 1). This method allowed us to obtain self-standing nanofibrous electrodes with ultra-low Pt loading ($0.05 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$), showing high activity towards the O_2 reduction reaction and electrochemical surface areas as high as $140 \text{ m}^2 \text{ g}^{-1}$.

In this work the morphological, structural and electrochemical characterization of these nanofibrous electrodes will be presented and discussed.

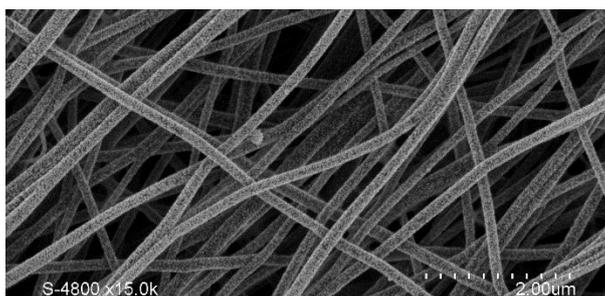


Figure 1: SEM micrograph of a nanofibrous electrode.

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ORAL O13:

STEAM ELECTROLYSIS USING PROTON CERAMIC CELLS AND MODULES – DESIGN AND PERFORMANCE MODELLING

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Proton ceramic electrolyzers (PCEs) have the potential to produce dry hydrogen directly from steam, utilising renewable energy including heat from for instance solar or geothermal sources. Such electrolyzers will have significant operational differences from for instance solid oxide electrolyzers (SOEs) and polymer-based electrolyzers.

In the FCH-JTI project ELECTRA we develop components, tubular cells, and modules for testing PCEs. The work comprises design and balance of plant considerations as well as modelling of operation and performance of modules and entire plants, based on project-generated and external data.

Results from these on-going modelling studies will be presented and discussed, emphasising the integration of thermal energy sources, cost considerations, and comparisons with solid oxide and polymer-based alternatives.

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621244 (ELECTRA).

ORAL O14:
**Anode performance based on high temperature proton conducting
electrolysers and a multitube module construction**

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The use of high temperature electrolysers (HTE) of steam offers high efficiency of conversion of renewable and peak electricity to H₂. In solid oxide electrolysers (SOECs), that use oxide ion conducting electrolytes and operate at around 800 °C, the hydrogen is produced on the steam feed side. However, in proton conducting electrolysers (PCECs) a high temperature proton conducting electrolyte is used instead and protons are pumped and form dry H₂, leaving O₂ on the steam side. These PCECs can produce pressurized dry H₂ directly.

La_{0.8}Sr_{0.2}MnO_{3-δ} (LSM) composite anodes have been deposited on proton-conducting BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-δ} (BCZY27) electrolyte and studied in symmetric cells to investigate the anode microstructure and electrochemical performance. EIS measurements were performed in the 800 - 500 °C range under 3 bar of pressure of wet air (75% of steam).

After the first screening, LSM/BCZY27 electrode composite, was prepared by mixing a vol.% of each phase and sintering at 1100 °C/2h. LSM/BCZY27 50-50 vol.% showed the best performance being the polarization resistance 6.04 Ω·cm² at 700 °C and high steam pressure (0.75 bar of air and 2.25 bar of steam).

Then, the electrode layers were infiltrated by dropping a water solution of different catalytic nanoparticles on each side of the electrolyte to improve the catalytic activity, such as, Pr, Ce, Zr and Pr-Ce. The infiltrated cells were fired at 850°C for 2h to obtain the desired crystalline phase of each one and measured in a three-wire configuration, imposing different currents. The R_p showed the best results (< 0.2 Ω·cm²) applying a density current of 0.5 – 5.5 mA/cm² range.

Finally, all these materials will be tested in a new concept of the Tubinder multi-tubular-cell for HTE use. ELECTRA will refine the design and then produce it. This will for the first time demonstrate the possibility of monitoring tightness and controlling working conditions of individual tubes, from a cold side plenum. The module is at present design stage providing for a cylinder reactor with several tubes able to produce 250 Ln/h of H₂ from 1 kW of electrical power.

ORAL 015:
MANUFACTURING OF THIN FILM METAL SUPPORTED PCECs

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High temperature electrolysis (HTE) may be based on electrolytes with either oxide ion (SOEC) or proton conductors (PCEC). Proton conductors are advantageous yielding dry hydrogen at a lower operating temperature than their counterparts. This alleviates need for gas drying, increases component stability and enables easy integration with waste heat from industry. Introduction of thin film electrodes and proton conducting electrolyte on a metal support (MS-PCEC) opens up for reduced cost, better thermal conduction (reduce thermal stresses) and possibility for additional reduction in temperature of operation (ITE) due to the reduced resistance of thin film functional layers. PCEC also avoids steam corrosion of the metal support and oxidation of the Ni electrode since pure dry H₂ is produced at the metal support side.

Manufacturing processes for planar metal supported PCECs (MS-PCEC) are developed at SINTEF and UiO, enabling the fabrication of complete single PCEC cells using scalable and flexible techniques, such as tape-casting, spray-coating and pulsed laser deposition (PLD). Low cost ferritic stainless steel powder from Höganäs was used to develop robust metal supports with homogeneous pore distribution and sufficient strength when sintered at 1150 °C. Coatings have been developed to protect the metal support during the fabrication steps. Using low temperature methods like PLD to deposit thin films of a Ni-BZY cermet and a BZY electrolyte requires smooth surface. A smooth intermediate ceramic layer with surface roughness of ~3–5 μm was successfully made at 1175 °C under reducing conditions, having the required strength, smoothness and microstructure. A protocol for deposition of Ni-cermet electrode and dense electrolyte layers on the MS/ceramic using PLD was obtained. The cells were tested using Pt as anode showing promising results, with a resistance of some ohms at 750 °C. The resistance was higher at lower temperature since the resistance of the contact layer is still too high.

ORAL O16:
**Performance and durability of Solid Oxide electrolyser stacks for hydrogen
and syngas production**

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The Fuel Cell team at VTT Technical Research Centre of Finland Ltd. focuses in the development of low and high temperature fuel cells (PEMFC and SOFC) and in hydrogen and syngas fuel production via electrolysis. During its ten years of existence, the Fuel Cell team has developed considerable know-how in experimental and modelling tools and built extensive research infrastructure. Important demonstration projects included stationary 10 kW SOFC [1], 50 kW PEMFC fuel cell systems [2] and a hybrid fuel cell forklift [3].

The work presented here focuses on characterising the performance and durability of two Solid Oxide Electrolyser short stacks. The 500 W electric stacks were stack prototypes produced by SOLIDPower, Italy. The performance was characterized as a function of temperature and CO₂ fraction (from 0 to 0.45). Cathode outlet gas analysis carried out by microGC indicates good match between the measured and the expected compositions according to thermodynamic equilibrium. This result indicates that the water gas shift reaction is at equilibrium in the tested range.

Long-term durability tests were performed at 750°C for durations of 1500 h and 2300 h at current density between 0.5 and 0.8 A/cm². The first stack exhibited no degradation in steam electrolysis during the whole test duration, on the contrary the voltage improved at a rate of 9 mV/kh. The second stack also exhibited activation for the first 1700 h. Then, however, the tendency reversed and degradation rate of 41 mV/1000 h was measured until the end of the test at 2300 h. If the reason behind the activation is not clearly understood yet, these results show the necessity to conduct sufficiently long durability test because of possible transient effects that affect the degradation rate measurement. The CO₂ inlet fraction was varied during the durability test of the second stack. It appeared that the addition of CO₂ did not correlate with an increased degradation rate. This result is encouraging and indicates that this stack is a suitable candidate for co-electrolysis operation.

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621173.

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ORAL O17:
**OPTIMUM AMOUNT OF FUEL ELECTRODE POROSITY FOR AN
INTERMEDIATE TEMPERATURE SOLID OXIDE ELECTROLYZER
CELL**

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Among all the components of solid oxide electrolyzer cell (SOEC), the fuel electrode plays an important role in the reduction of H₂O to produce H₂. It acts as the main site for the reaction products removal through the whole fuel electrode to avoid concentration polarization as well as provide essential electrical conductivity to decrease ohmic polarization. The porous structures of fuel electrode have been proposed to fulfil the cathodic functions of SOEC, for further improvement of the performance of the cells. In this academic research, Ni-YSZ, SDC-YSZ and SDC-BSCF are chosen as the fuel electrode, bi-layer electrolyte and composite air electrode, respectively. In order to enhance the fuel electrode and so the electrolyzer cell performance, 5 wt.%, 7 wt.%, and 10 wt.% of graphite, as the pore former, are added into the Ni-YSZ fuel electrode material and 18%, 23%, 33%, and 40% porosity are achieved in the Ni-YSZ fuel electrode structure, respectively. The sample with 33% fuel electrode porosity which shows the highest performance among all the investigated cells has the optimum amount of fuel electrode porosity for the Ni-YSZ/YSZ-SDC/BSCF-SDC solid oxide electrolyzer cell. These results are in good agreement with both microstructural and impedance study of the cells.

ORAL O18: STEAM INJECTION FOR ELECTROLYSIS EXPERIMENTS AND HYDROGEN RECOVERY WITH SOFT MICA AS SEALING

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Fiaxell has been active since 2008 in the field of Solid Oxide Fuel Cells (SOFC) and has been developing components for SOFC research, such as anode supported cells, the 2R-Cell, able to withstand full re-oxidation and thermal cycles, in comparison to the standard commercial ASC cell destroyed after only one redox cycle. The 2R-Cell is robust and has demonstrated high fuel utilization (85-90%) and electrical efficiency till 50% with pure hydrogen on button cells.

In order to test SOFC/SOEC cells, Fiaxell has developed the Open Flanges™ Set-Up, that allows researchers to do various experiments, such as electrolysis, co-electrolysis, in situ gas processing (POX, SR), polarization and impedance spectroscopy measurements.

In SOFC mode, the Open Flanges™ Set-Up allows characterization of fuel utilization and electrical efficiency on small or large cells. The measurements can be carried out with or without sealing.

In the case of electrolysis and particularly of co-electrolysis of water and CO₂, gas recovery becomes necessary in order to analyze the gas composition, such as CO/H₂ ratio in the exhaust.

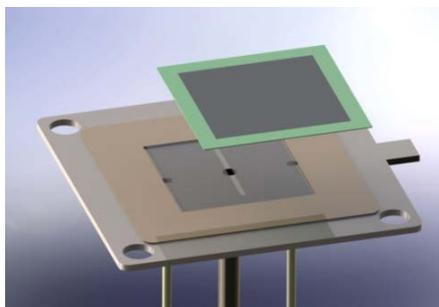


Fig.1: Soft mica sealing (beige) on the gas diffuser plate

For this kind of experiments, a new type of soft mica sealing material was investigated (Fig.1).

Different parameters were studied, such as squeezing versus compression pressure (Fig.2), gas recovery as a function of substrate porosity (steel sheet as blank, electrolyte and anode supported cell) and gas mixture (Fig. 3).

As shown on Fig. 1, the seal material is set up directly on the diffuser plate and can be removed easily, contrary to glass-based sealants that necessitate thorough and time consuming grinding.

For steam injection, an integrated steamer has been developed, allowing a homogenous production of steam without the need of external evaporator and heated line to avoid condensation. The steamer is simply plugged

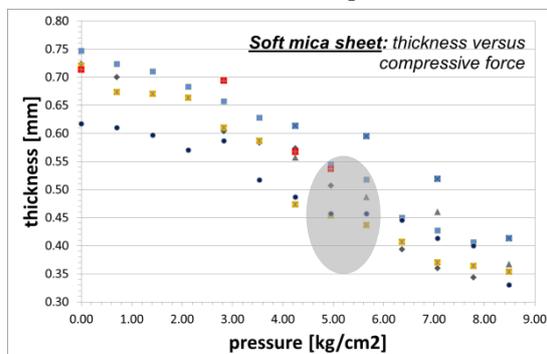


Fig.2: Soft mica sealant thickness as a function of compression force. The grey circled area indicates the acceptable operating pressure on the system. The results of six experiments show the variation in repeatability.

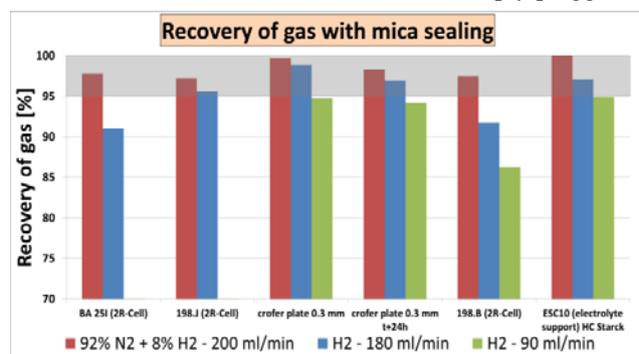


Fig.3: % recovery of exhaust gas using soft mica sealing with different configurations (blank steel sheet, anode and electrolyte supported cell supported cell, gas mixture and flow rate).

into the set-up and connected to the peristaltic pump to control the micro flow rate. By using the set-up heat, the liquid (water, NH₃, ethanol, methanol or any other liquid fuel) evaporates smoothly to produce a steady flow of steam or gas which feeds directly the fuel or air electrode (in the case of protonic conductors). Moreover, the steamer also facilitates co-electrolysis where CO₂ and steam are mixed in the device, providing a stable flow to the cell [1].

Keywords: SOFC, SOEC, mica, glass sealant, co-electrolysis, soft sealing, fuel cell, gas recovery, anionic, protonic conductors, steamer, POX, SR, CO₂, H₂, ASC, anode supported cell.

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ORAL O19:
STEAM ELECTROLYSIS USING PROTON CERAMIC CELLS

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With the recent introduction of hydrogen-fuelled vehicles in major markets there is an increased demand to develop new cost-efficient technologies for clean and renewable hydrogen production. High temperature electrolyzers (HTEs) may produce H₂ efficiently utilising electricity from renewable sources and steam from solar, geothermal, or nuclear plants. The traditional solid oxide electrolyser cell (SOEC) leaves wet H₂ at the steam side. In contrast, proton ceramic electrolyser cells (PCEC) can pump out and pressurize dry H₂ directly. Further, the danger of delamination of oxygen electrodes due to O₂ bubbles in SOECs is alleviated in PCECs. In the literature we find some reports using various solid solutions of the BaZrO₃-BaCeO₃ system (BZCY) as the electrolyte, with promising current densities. However, relatively high polarization resistance of the O₂/H₂O-electrode and non-faradaic electronic leakage currents are challenges that are not properly understood nor quantitatively described.

In this contribution, we investigate a cathode-supported tubular proton ceramic electrolyser cell using a 30 μm BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-δ} electrolyte with a Ni-BZCY composite as the cathode (H₂-electrode) and the double perovskite Ba_{1-x}Gd_{0.8}La_{0.2+x}O_{6-δ} (x = 0-0.5) as the anode (H₂O-O₂ electrode). Current-voltage characteristics and hydrogen production rates are measured as a function of steam pressure (*p*H₂O = 0.5-3 bar) and *p*O₂ in the temperature range 500-700°C. Combined with electrochemical impedance spectroscopy under electrolysis operation we are able to describe the functional dependencies of the electrodes and the electrolyte separately.

Acknowledgements: The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621244.

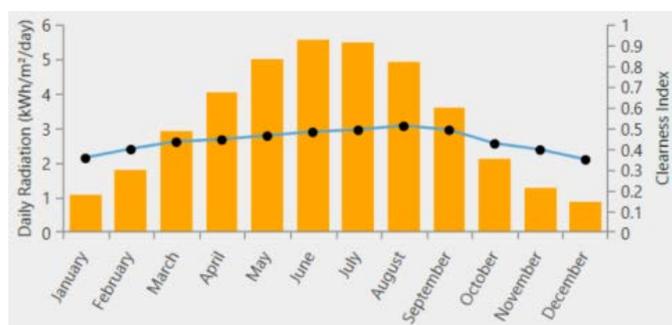
ORAL O20: USING HYDROGEN STORAGE TO REACH SELF-SUFFICIENCY

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Introduction

Providing reliable electric power supply using only solar resources is not possible due to the variability of the global horizontal irradiance, especially for countries above the tropics. For example, here under is the GHI for Nantes. Using batteries to store enough energy is impossible, batteries are made to store energy for less than one week.



Solution by PowiDian

Powidian, with its SAGES technology, use a complete hydrogen chain (Electrolyser, Pressure storage, Fuel Cell) to store enough energy during the time it is available to use it when needed. The complete system consists of a renewable resource (sun in this case) linked with a battery bank and hydrogen storage. The system is working since one year in the French alps at 2600m high.

In this case, the available place for PV panel was too small to reach the needed power during the opening of the haven (during summer), place limited by the environmental laws (natural park). The aim of this system was to install a system able to produce and store energy during closed time (winter) to use it 3 months later.

Storage: Batteries VS Hydrogen

Batteries, with their roundtrip efficiency compared with the global efficiency of electrolyze and fuel cell, will not be replaced by hydrogen storage for power to power for very short time. The two technologies are complementary, batteries for short term storage (<3 days) and hydrogen for long term storage, in replacement of diesel generator used before.



This technology has been chosen by EDF (French electricity provider) to test hydrogen storage for remote communities in Mafate Circus in the Reunion Island.

ORAL O21: Preliminary design of a wind driven vessel dedicated to hydrogen production

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Currently, the worldwide renewable energy capacity is mainly composed of onshore wind energy and solar energy. In 2015, renewables contributed to 19 % of the humans' global energy consumption [1]. To reach the target of limiting global warming to 2° C between now and 2100, it is then necessary to continue the development of renewable energies. Most recently, offshore wind energy capacity grew significantly, especially in Northern Europe with bottom-fixed foundation and may significantly contribute to the worldwide electricity production in a near future. Along with the development of renewables, it is also necessary to find alternatives to fossil fuels. These alternatives could be biofuels, electric vehicles with storage system or electric vehicles using fuel cells and hydrogen. This is the scope of the present work with the presentation of preliminary results about the design and performance of an original concept for the conversion of offshore wind energy into hydrogen.

The working principle is relatively simple: wind is used to propel a ship, a hydro-generator converts the ship's kinetic energy into electricity and the generated electricity is converted into hydrogen. The concept is not new actually since the first patent about such a system was filled in 1982 by Salomon [2]. However, scientific investigations on the concept started only recently [3, 4]. The main differences among those works are in the means used to convert wind energy into thrust force. Kim investigated the use of kites whereas Peltz investigated the use of air foils.

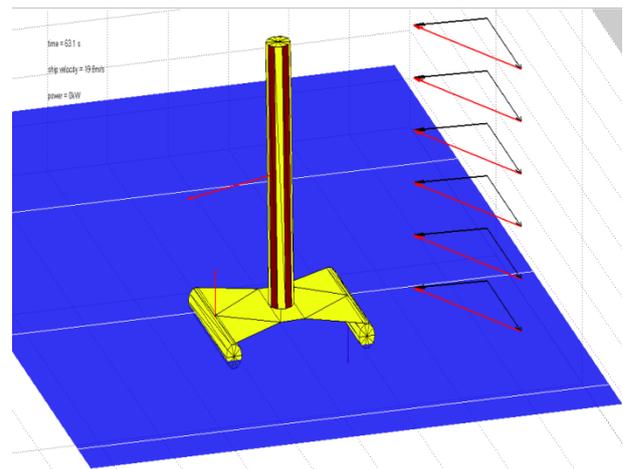


Figure 1. Picture of the wind-driven hydrogen producing vessel at static equilibrium

In this study, we consider the use of a Flettner rotor. A model of the hydrogen producing vessel is developed based on existing data for high performance vessel hulls and lift and drag coefficients for the Flettner rotor [], Figure 1. The design is optimized with respect to the axial induction velocity through the water turbine disk. Results indicate that a rather small vessel could produce significant amount of hydrogen.

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ORAL O22:
Applications of Energy Storage Systems for offshore wind production

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ORAL O23:
**CONTRIBUTION OF OCV MEASUREMENTS DURING START-UP
AND SHUT-DOWN PROCEDURES TO THE SOH ESTIMATION OF A
H₂/O₂ PEM FC STACK: DEVELOPMENT OF ORIGINAL INDICATORS
FOR THE INTERNAL H₂ LEAK ESTIMATION**

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The durability concern about Proton Exchange Membrane Fuel Cell devices is today one of the main sources of investigation in the PEMFC community: the too short lifespan of PEMFC devices limits the expansion and spreading of the technology through potential markets. Among other degradation roots responsible for these short lifetimes, the growth of the internal leak between the H₂ and the Air/O₂ compartments, linked with the membranes ageing, often appears as one of the most important causes of failure in PEMFC devices [1]. The monitoring and diagnosis of the internal leak throughout the life of the PEMFC device is thus crucial, to have a relevant State Of Health assessment. A certain amount of diagnosis technics already exist to evaluate the internal leak in a PEMFC stack at the stack and at the cell level [2].

In some of these methods, specific sequences are applied to the PEMFC device and/or the PEMFC device is used in a specific configuration (as in cyclic voltammetry measurements for example) to extract an SOH indicator related to the internal leak evaluation [3].

A compromise between the constraints of the diagnosis method in a real-life environment and the accuracy of the method to evaluate the SOH is then to be done: higher accuracy in the evaluation of the SOH requires methods less adapted to a real-life context while methods more adapted to such a real-life context often present less accuracy in the evaluation of the SOH.

The purpose of this work is to investigate the routine procedures of a PEMFC stack life (start-up, shut-down) in order to look for original indicators for a first step diagnosis of the internal leak. An 8000h ageing campaign were carried out on a 10 cells H₂/O₂ PEMFC stack from Areva Energy Storage under constant current solicitation. Correlations will be underlined between voltage measurements in open circuit operation during the routine procedures and the internal leak evolution through the campaign. A discussion will be then introduced about the potentialities to assess a first level of SOH estimation for a PEMFC stack through the exploitation of these routines.

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ORAL O24:

ANODE SUPPORTED SOFC ON METALLIC FOILS

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Planar anode supported SOFC are the most available cells. Metal supported cells offer advantages in thermal cycling. An intermediate solution has been developed which permits to avoid non-separable units sealed with melted glass. A classical cell is inserted in a metallic foil with a special ceramic bond between the metal and the electrolyte layer. So the loads required by the electrical contact and the hermetic joining of the stack could be nearly independent. Several designs have been simulated from cold formed foils of low thickness to thicker engraved sheets. Crofer 22, AISI 430 and 441 have the thermal expansion coefficients matching the best the cells coefficients. Other metals have been investigated as thermal expansion can be compensated by the foil elasticity. Strain, stress and thermal expansion have been modelled with the COMSOL Multiphysics® software under linear elastic conditions. Results are presented in stationary and time dependent conditions. Considering that heat transfer and mechanical equations are not coupled, heat is simply generated by the Joule heating in the cell. So the temperature field is determined by linear conduction equations which facilitate the simulation of numerous designs by finite element software. Combining planar SOFC with a small metallic support permits to dismantle the stacks without destruction of the cells. The principle can be applied to SOE.

Proton Exchange Membrane Fuel Cell Diagnosis by Spectral Characterization of the Electrochemical Noise

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Keywords: Electrochemical noise analysis, Power spectral density, Diagnosis, PEMFC

Recently, there is an active tendency of research, development and adoption of new energy sources. One of the most perspective system, in this area is the proton exchange membrane fuel cell (PEMFC). Polymer electrolyte membrane fuel cell (FC) is potentially beneficial for a wide range of applications, thanks to its attractive advantages, such as high efficiency, high power density, zero greenhouse gases emissions, low temperature range 50-80 °C operation [1]. However there are still two barriers: the **reliability** and **durability**, which block the wide application of PEMFC. Fault diagnosis can be an efficient solution to overcome these barriers. In this condition the method based on informational properties of electrochemical noise is promising [2]. Indeed it allows to develop diagnostic systems without perturbation of FC in operation mode. In frame of the present work, electrochemical noise analysis (ENA) was applied to study the effect of the relative humidity and current density in a single PEMFC cell. It has been found that diagnostic features can be extracted by the Power Spectral Density (PSD) of the FC electrochemical noise. The PSD of electrochemical noise versus frequency for FC operated under constant current mode (8 A) is presented in Fig(1). It was revealed that in low frequency range ($f < 100$ Hz) the fluctuation has a flicker noise nature $1/f^\alpha$. PSD highlighted a linear slope (Flicker noise) of $\alpha = 2$ for all relative humidities except RH = 20/20. When the membrane is under dry conditions (RH = 20/20), PSD shows a different signature with slopes behavior divided in three parts ($\alpha = 1.63, 3.98$ and 1.82). In conclusion, ENA is very sensitive to changes of operating conditions of the FC and PSD calculations can be a powerful tool for the detection of an incorrect water balance (drying and flooding).

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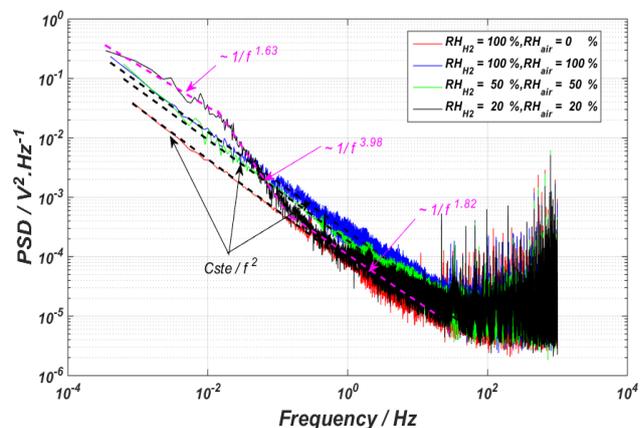


Fig. 1. Power Spectral Density of PEMFC voltage fluctuation during 2 hours.

ORAL O26:
**USING THE CHANNEL IMPEDANCE TO MEASURE AIR
VELOCITIES IN POLYMER ELECTROLYTE MEMBRANE FUEL
CELLS**

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Polymer Electrolyte Membrane (PEM) fuel cells are considered as promising clean sources for automotive applications. A key challenge to reduce the cost of this technology is to increase the power density by operating PEM fuel cells at high current densities without significantly increasing the electrical consumption of the auxiliaries, such as the air feeding system. The energetic cost of these auxiliaries can represent more than 20% of the energy consumed by a fuel cell system, therefore air flow rates are usually kept as low as possible, i.e. air stoichiometric ratios ranging between 1.5 and 3. In a stack configuration, such low stoichiometries may induce a maldistribution of air flow rates from the manifold to each single cell. Therefore, the knowledge of the air velocity that flows through each cell of a stack would be a valuable criterion to diagnose the maldistribution of air and to prevent the fuel cell channel clogging.

Using Electrochemical Impedance Spectroscopy (EIS) when a PEM fuel cell operates in low air stoichiometry, several studies have reported the measurement of the channel impedance at very low frequency (ranging from 5 to 0.1 Hz) [1]. In this communication, we will present how this channel impedance can be used to measure air velocities in fuel cell channels [2]. From the equations of the oxygen transport in fuel cell channels, we derive an analytical expression for the channel impedance at low frequencies which is a function of the operating conditions, the channel geometry and air velocity only. Air velocities are computed using a nonlinear curve fitting which compares the channel impedance computed by our model to the single cell impedance measured at current densities ranging from 0.16 to 0.5 A/cm² under various air stoichiometry conditions. Our results show less than 13% of relative error between the theoretical air velocities given by the mass flow controller and those measured from the fuel cell channel impedance for current densities lower than 0.42 A/cm². A direct application of this work is the real-time diagnostic of fuel cell channel clogging in stack configuration.

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ORAL O27:

FROM GAS PRODUCTION TO DIRECT ELECTRICITY PRODUCTION BY COUPLING OF A GASIFIER AND A NICKEL/YTTRIA-STABILIZED ZIRCONIA-BASED SOLID OXIDE FUEL CELL.

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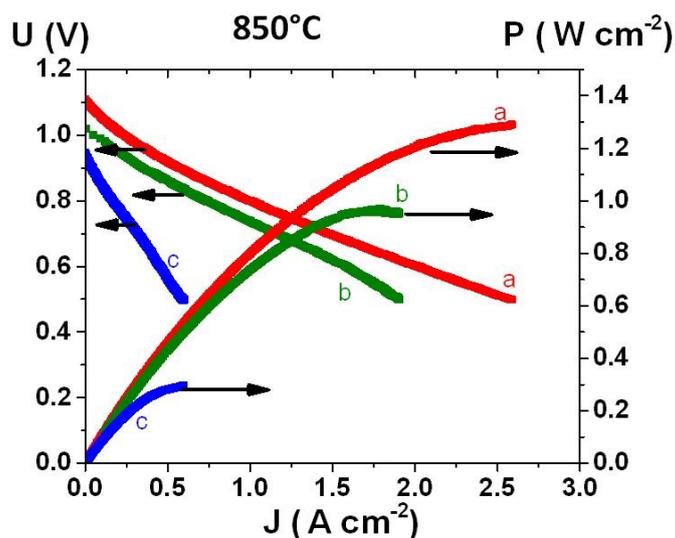
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This work presents the direct coupling of a gasification pilot according to the patented concept by S3D Company and of a Ni-YSZ-based SOFC. The composition of gas issued from the gasifier is rather stable, with $H_2 \approx 14\%$, $CO \approx 14\%$, $CO_2 \approx 22\%$ and $N_2 \approx 47\%$, and depends directly from wood injection conditions.

Before injecting directly the gas on the cell, a home-made cell consisting of an industrial Fiaxell Nickel/Yttria-stabilized Zirconia-based anode-electrolyte assembly covered by praseodymium oxide was performed with H_2-N_2 mixtures. The cell is tested at 750° and $850^\circ C$, with a maximum power density of $1.4 W cm^{-2}$ at $850^\circ C$ when fueled with a 76% - 24% H_2 -Ar mixture.

Then, using exclusively the fuel issued from wastes, without any additional purification steps, maximum power densities of $340 mW cm^{-2}$ and $113 mW cm^{-2}$ can be obtained at $850^\circ C$ and $750^\circ C$ respectively. Differences between performances obtained with diluted H_2 - CO mixtures and fuel issued from the gasifier are interpreted as depending on the H_2S content of the syngas.



Voltage and power density versus current density characteristics recorded at $10 mV s^{-1}$ under air on the cathode side and under wet (3% H_2O) 76% H_2 -24% Ar mixture (a), 37% H_2 -63% Ar mixture (b), and bag mixture (c).

ORAL O28:
PROTON CERAMIC ELECTRODICS

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Proton ceramic fuel cells (PCFCs), electrolyzers (PCEs), as well as other proton ceramic electrochemical cells (reactors, pumps, compressors) have several advantages from the pure protonic transport. In reality, however, the situation is often more complicated than for cases with oxide ion transport, especially regarding electrodes, where literature is still sparse.

In the present contribution, we define and distinguish the hydration reaction that provides protons in the electrolyte, and the electrode reactions for protons on the reducing and oxidising sides.

We next identify likely reaction steps for the redox reactions on hydrogen and oxygen side electrodes, typically metallic and ceramic, respectively. We distinguish transport through bulk (requiring mixed conducting electrodes and utilising 2-dimensional interfaces for charge transfer) and transport on surfaces (utilising 1-dimensional triple phase boundaries).

We suggest analytical expressions for the contributions to the impedance of the electrode: bulk, grain boundaries, space charge layer at the electrolyte/electrode interface, charge transfer, and mass transport, showing how impedance spectroscopy vs temperature and partial pressures of reactants and products can yield information about active microstructural regions and of rate determining steps in the reactions.

We finally touch upon voltammetry for additional information, and test under realistic operational conditions.

Acknowledgements: The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621244, and from the Research Council of Norway through the PROTON (225103), FOXCET (228355), and ROMA (219194) projects.

ORAL O29:

Optimization of the doped ceria as interlayer between the electrolyte and the SOFC oxygen electrode: electrochemical studies

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The main issue during the ageing of commercial SOFC single cells is the reactivity of the materials at the operating temperature. Typically, the cation migration that especially occurs at the cathode side leads to the formation of parasitic phases, which results in an increase of the overpotential. To overcome this problem, a thin interlayer ($\approx 2\text{-}3\ \mu\text{m}$) made of gadolinium or yttrium doped ceria (namely GDC or YDC) is usually added between the cathode material and the electrolyte (typically YSZ, Ytria Stabilized Zirconia).

This work is devoted to the study of the OER (Oxygen Electrode Reaction) for $\text{La}_2\text{NiO}_{4+\delta}$ (LNO) cathode deposited on a 3 mol.% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (TZ3Y) dense electrolyte, covered with a barrier layer made of either $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.90}$ (GDC) or $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}$ (PrDC).

For LNO//GDC//TZ3Y symmetrical half-cells, Gerischer impedance arcs are measured by electrochemical impedance spectroscopy: they are accurately fitted using the Adler-Lane-Steele (ALS) model. Surprisingly, the value of the polarization resistance of the half-cell is shown to depend on the GDC sintering temperature ranging from 1200 °C to 1450°C. Detrimental interdiffusion at the GDC//TZ3Y interface gradually increases with the temperature, which affects the series resistance of the half-cell. In addition, interdiffusion at the LNO//GDC interface affects the overall ionic conductivity of the electrode. Finally, the polarization resistance of an electrode//electrolyte architecture does not only depend on the intrinsic electrochemical performances of the electrode, but is also largely influenced by the interfacial area between the electrode and the electrolyte, which may act like a bottleneck for the oxide ions from LNO electrode toward the GDC interlayer, and *vice-versa*. Optimal thermal conditions for manufacturing the GDC/LNO electrode are proposed [1].

The praseodymium doped ceria (PrDC) is proposed as an alternative interlayer [2]. Even though some reactivity occurs between PrDC and TZ3Y, the formed compounds seem to efficiently conduct the oxide ions, and therefore favour the ORR. Besides, a low reactivity is detected between LNO and PrDC. As a result, the total resistances, *i.e.* series and polarization resistances obtained with a LNO//PrDC//TZ3Y half-cell in the temperature range 500 – 800 °C are much lower than those obtained with a LNO//GDC//TZ3Y half-cell, sintered in the same conditions.

Finally, differences in the shape of the impedance arcs are observed depending on the interlayer composition (GDC or PrDC): this feature is discussed.

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ORAL O30:
**ADVANCES IN THE UNDERSTANDING OF THE ENHANCED
CONDUCTIVITY IN CARBONATE/OXIDE COMPOSITES AS
ELECTROLYTE FOR SOLID OXIDE CELLS**

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Composites made of a mixture of carbonates and oxides have attracted new interest because of their high ionic conductivity, reaching 0.1 S.cm^{-1} at temperatures even lower than 600°C . Thus their use as electrolyte materials in solid oxide fuel cells has been considered by several authors, showing power densities up to 1 W.cm^{-2} . Only short terms performances are reported in the literature. Initially suggested and developed by Bin Zhu[1], the origin of such elevated conductivity is still controversial, mainly to determine precisely whose species and mechanisms are involved. Thus a lot of works have been dedicated to systematic experimental studies. Despite numerous parameters studied, experimental approach is not enough to fully elucidate them even if the interface between oxide and carbonate phases is clearly identified to be the main responsible, acting as “a superionic pathway”.

The present work is a review of the experimental results we obtained in our group since several years by impedance spectroscopy[2-4], enriched by a theoretical approach in parallel. We've been studying the impact of the oxide phase (YSZ, ceria-based, TiO_2) and the carbonate (Li-Na and Li-K eutectics) conductivity on the composite conductivity, as well as the operating atmosphere (oxidizing and H_2 -based reducing atmospheres) and the stability during cycling or aging. Because of peculiar behaviors, we recently initiated DFT calculations in order to model the carbonate/oxide interface. The first results allowed us to build several interfaces, from the most stable surfaces of carbonates and oxides determined separately[5-6]. The model was validated through the reconstruction of IR and Raman spectra, compared to experimental ones we obtained also in our group. DFT calculations showed that the carbonate phase is less ordered at the interface than in the carbonate bulk, yielding to easier reactivity with YSZ. Additional and complementary data have been obtained by thermal analysis (TGA/DTA) and gas chromatography coupled to mass spectrometry to provide new elements in the understanding of this enhanced conductivity in carbonate/oxide composite.

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ORAL O31:
**Neutron diffraction as a characterization tool
of SOFC materials under operating conditions**

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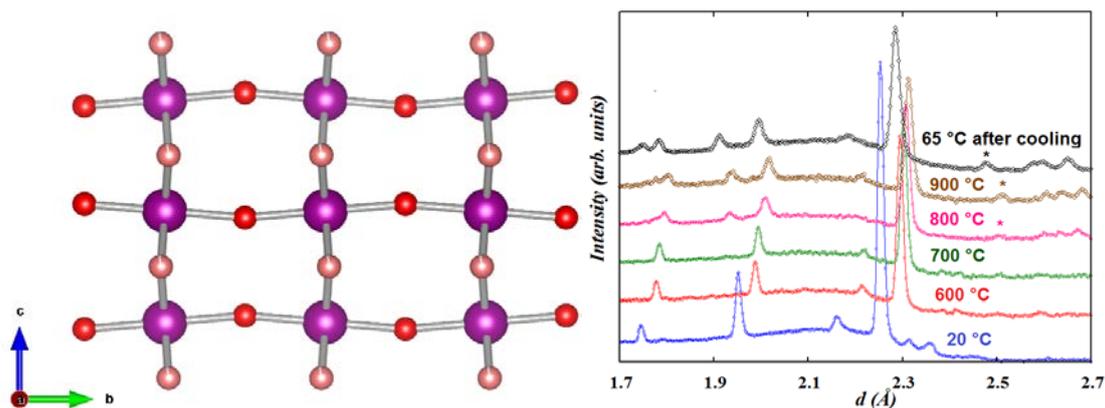
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Non-stoichiometric transition metal oxides with mixed ionic and electronic conductivity are currently studied due to their potentiality as Solid Oxide Fuel Cell (SOFC) electrode materials. A better characterization of their redox behavior and structural stability in operating conditions as well as the determination of the mechanisms of oxygen diffusion contribute to the development of advanced SOFC materials.

We will describe recent examples of neutron diffraction in the field of solid electrode materials. Data collected *in situ* as a function of temperature on the high-flux POLARIS diffractometer at ISIS (RAL, UK) exploited the sensitivity of neutron to light atoms to determine atomic positions and site occupancies of oxygen in simple/double perovskite oxides, $Ln_{0.5}Ba_{0.5}BO_{3-\delta}/LnBaB_2O_{5+\delta}$ (Ln = lanthanide, B = transition metal). Problems related to oxygen vacancy intercalation/deintercalation, octahedral tilting, phase transitions, order–disorder phenomena, charge and orbital ordering and detection of intermediate phases as well as oxygen diffusion path are addressed.



View of the distorted structure of the A-site disordered manganite at 20 °C and selected region of neutron diffraction data highlighting the structural A-site disorder → order phase transition.

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Effect of doping level x in $\text{Ln}_{1-x}\text{M}_x\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ SOFC anodes

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There is an increasing demand for the development of alternate anode materials with improved tolerance towards carbon deposition and sulfur poisoning to improve the fuel flexibility and efficiency of Solid Oxide Fuel Cells (SOFCs) [1]. In this sense, perovskites have gained attraction as electrode materials for SOFCs due to their catalytic, ionic and electrical conductivities, chemical and thermal stabilities at higher temperatures [2,3].

Several studies based on perovskites have shown that changes in physical properties are related to changing doping level x of the A-site. However, these physical properties can vary even at a constant value of x [4], being very sensitive to changes not only in the doping level (x), but also in the average size of the A cations ($\langle r_A \rangle$), and in the effects of A cation size disorder ($\sigma^2(r_A)$) quantified as $\sigma^2(r_A) = \langle r_A^2 \rangle - \langle r_A \rangle^2$ [5-7].

In this study, we investigate the variation of the doping level x in the structure and electrical properties of a series of $\text{Ln}_{1-x}\text{M}_x\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ ($\text{Ln} = \text{La}$ y/o Nd ; $\text{M} = \text{Sr}$ y/o Ca ; $x \leq 0.25$) perovskites. This has been achieved by keeping the mean ionic radius $\langle r_A \rangle$ (1.22 Å) and the cation size disorder $\sigma^2(r_A)$ (0.0001 Å²) constant throughout the whole series of compositions prepared.

The samples are prepared using the urea combustion method. X-ray powder diffraction (XRD) shows that all of the compounds have orthorhombic symmetry (space group: Pnma). The structural, morphological and electrical properties are highly dependent on x ; a systematic decrease in unit cell volume, increase in grain growth and decrease in electrical conductivity (in reducing atmosphere) is observed with increasing doping level.

Acknowledgements: This research has been funded by the Ministerio de Economía y Competitividad (MAT2013-42092-R) and Dpto. Educación, Política Lingüística y Cultura of the Basque Government (IT-630-13). The authors thanks the support received by the European Regional Development Fund. (ERDF). SGiker of UPV/EHU technical support is gratefully acknowledged. A. Wain thanks Ministerio de Economía y Competitividad for funding his work (BES-2014-068433).

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ORAL O33: IMPEDANCE SPECTROSCOPY OF SOFC CATHODES : SOME EXAMPLES

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The importance of Electrochemical Impedance Spectroscopy (EIS) is illustrated in this communication by three studies of cathode behavior in half SOFC cells (cathode/electrolyte/cathode). The electrolyte is a Ce_{0.9}Gd_{0.1}O_{1.95} (GDC) ceramic. The cathode is a bi-layer of a porous thick film of La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} (LSCF) on top of a dense thin LSCF interlayer. The EIS measurements were made between 0.05 Hz and 10⁶ Hz with an AC voltage of 100 mV and from 500 to 700 °C [1]. All EIS were validated with a Kramers-Kronig test. Data analysis was performed with the Complex Nonlinear Least Squares (CNLS) software 'EqCwin95' [2], using an 'equivalent circuit' based on electrical analogues, such as resistance (R), inductance (L), capacitance (C), diffusion related dispersion relations and the ubiquitous constant phase element (Q).

1/ Influence of AC-voltage amplitude

The amplitude of the applied AC-voltage can have a significant influence on the impedance. This has been tested with a range of voltages up to 2000 mV. Above 500 mV a change in the Nyquist diagrams is observed, mostly in the low frequency region. This is due to non-linear electrode behavior, which is confirmed by the CNLS-analysis based on a series arrangement of two (RQ) circuits (R in parallel with Q). Above 500 mV the low frequency R increases, while the high frequency R remains constant.

2/ Influence of cathode thickness

Three half cells have been prepared with porous LSCF cathodes: respectively 20, 40 and 60 μm thick. At 600 °C the CNLS analysis shows that the best fit of the impedances is obtained with three (RQ)'s in series for all three thicknesses. The most striking effect is the decrease of the resistances in low (R_{low}) and mid (R_{mid}) frequencies when the thickness increases, while the high frequency resistance (R_{high}) is less affected. The area specific resistance, ASR=(R_{low} + R_{mid} + R_{high})/2, decreases by a factor 1.7 from 20 to 40 μm and by a factor 1.25 from 40 to 60 μm. The corresponding relaxation times are independent of thickness. This indicates that the various oxygen reduction mechanisms are independent of the thickness of the porous cathode.

3/ Influence of temperature

From 500 °C to 700 °C, the Nyquist diagrams evolve for all cathode thicknesses. The CNLS analysis shows that, from 600 to 700 °C, R_{low} remains constant: this is a characteristic of gas diffusion limitation. Both R_{mid} and R_{high} show Arrhenius behavior from 500 to 700 °C, with R_{mid}>R_{high}. The activation energy of the ASR is the same for the three thicknesses with a value of 1.1 eV; this value is characteristic of the reduction of oxygen. The Distribution Function of Relaxation Times (DFRT, [3]) shows the same shape for the 40 and 60 μm thick cathodes, with three distinct peaks centered around 10⁻⁴ s, 10⁻² s and 1s. These peaks move slightly with temperature, whereas for the 20 μm cathode the three peaks move significantly with temperature.

The EIS analysis studies (2) and (3) indicate that the 60 μm thick LSCF cathode shows a better performance than the 40 μm or a 20 μm thick ones.

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ORAL O34:

A novel efficient oxygen electrode for Solid Oxide Fuel Cells: Pr₆O₁₁

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To increase Solid Oxide Fuel Cells performance, the optimization of the oxygen electrode is mandatory as its activation overpotential is usually higher than that of the hydrogen electrode. Finding new materials with mixed ionic and electronic conductivity is a good way to meet this goal.

In most of the current materials, the electrocatalytic properties are due to the presence of mixed valences of 3d cations, typically Fe^{3+,4+}, Co^{3+,4+}, Ni^{2+,3+}.

Praseodymium compounds exhibit excellent cathode properties, as for instance the nickelates Pr₂NiO_{4+δ} or Pr₄Ni₃O_{10±δ}, making them good candidates as oxygen electrodes material [1].

In this way, it was interesting to study the role of praseodymium cations in the oxygen reduction reaction.

The most stable praseodymium oxide is Pr₆O₁₁. Its mixed conductivity properties are first characterized; at 600 °C the oxygen diffusion coefficient value is as high as $3.4 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$, and that of the surface exchange coefficient is $5.4 \times 10^{-7} \text{ cm} \cdot \text{s}^{-1}$, which may lead to excellent electrocatalytic properties. Besides, the measured electronic conductivity is high enough for using Pr₆O₁₁ as a SOFC cathode.

Then, the electrochemical activity of Pr₆O₁₁ is characterized. As the phase undergoes several phase transitions upon increasing temperature, it is subjected to cracking or delamination if used as a regular screen-printed electrode. To avoid such problem, Pr₆O₁₁-based electrodes are prepared by infiltration. An aqueous solution of praseodymium nitrate is infiltrated into a Gd-doped ceria (GDC) backbone and fired at 600 °C to form a composite oxygen electrode Pr₆O₁₁/GDC. Electrochemical measurements show very low polarization resistance, $R_p = 0.028 \Omega \text{ cm}^2$ at 600 °C. A single cell made of a commercial Ni-YSZ/YSZ half-cell and of the infiltrated cathode is able to deliver a maximum power density of $825 \text{ mW} \cdot \text{cm}^{-2}$ at 600 °C. Ageing of this cell for 840 h, at 600 °C and $0.5 \text{ A} \cdot \text{cm}^{-2}$, shows a degradation rate lower than 1%, which allows concluding that this simple oxide is indeed a promising cathode material [2].

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ORAL O35:
**SYNTHESIS AND PROPERTIES OF DOPED $\text{Ba}_3\text{Ti}_3\text{O}_6(\text{BO}_3)_2$: A
 NEW SOFC ELECTROLYTE?**

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Solid Oxide Fuel Cells operate at high temperature (above 800°C) as they are limited by the ionic conductivity of the electrolyte. This high temperature has some drawbacks, like the necessity to use energy to heat the cell before operation, the faster ageing of cell's components and a longer starting time.

Nowadays, most studies on electrolyte materials for Proton Ceramic Fuel Cell (PCFC or H⁺ SOFC) focus on substituted perovskite-type oxides based on BaCeO₃, which present an excellent H⁺ conductivity level of 0.01 S/cm at about 600°C. Zirconia-based electrolyte shows an equivalent O²⁻ conductivity level but at higher temperatures. Lowering the operating temperature of SOFC down to 500-600°C range should permit to limit reactivity between the different materials and reduce premature ageing of the cell components.

IMN is recognized internationally for its prospective work on new electrolytes for SOFC, among them, H⁺ electrolytes such as BaIn_{1-x}Ti_xO_{2.5+x/2} compounds showing 3 mS/cm for x values between 0.1 and 0.2 at 450°C [1], and the original lanthanum oxyborate La₂₆O₂₇□(BO₃)₈. This later exhibits good protonic conductivity at 600°C [2] without any degradation of the mechanical properties of the ceramic through the hydration/dehydration process.

This work presents preparation of doped Ba₃Ti₃O₆(BO₃)₂ samples and characterization of their conductivity under air and reducing atmosphere. These results will be discussed in detail.

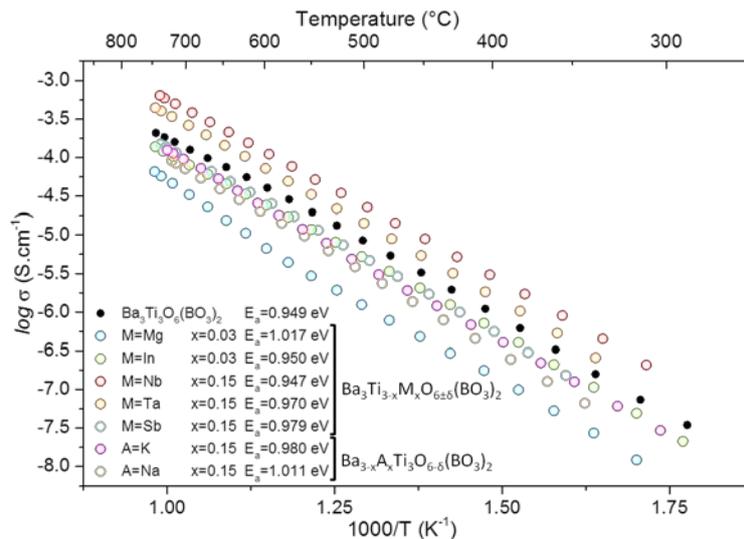


Figure 1: Ionic conductivity of eight prepared samples under dry air atmosphere.

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ORAL O36:
Deposition of ceria barrier layer by d.c. magnetron sputtering under reactive conditions

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The cells used in high temperature electrolysis and solid oxide fuel cell systems operate at about 700 or 800°C. At high temperature interfacial reactions between the yttria stabilized zirconia (YSZ) electrolyte and the doped-lanthanum cobaltites (LSCF) electrode lead to the formation of $\text{La}_2\text{Zr}_2\text{O}_7$ and/or the SrZrO_3 phases.

In this work, the sputter deposition of thin and dense gadolinia-doped ceria (GDC) interlayer was studied. This well-known material has a high ionic conductivity and permits to decrease the chemical reactivity between LSCF and YSZ [1,2]. The GDC barrier layers were sputter deposited on half cells manufactured by tape casting. Scanning electron microscopy (SEM) electron dispersive spectroscopy (EDS), Rutherford backscattering spectroscopy (RBS) and Raman spectroscopy were performed to analyze the main characteristics of the deposits. The influence of the manufacturing parameters as well as the effect of the pressure, the substrate temperature and the use of a substrate bias was studied. Finally, heat treatments were performed to ensure the stability of the deposited compound.

Presentation preference: Oral

Reference to a journal publication:

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ORAL O37:

Synthesis and corrosion mechanisms of $Y_{2-x}Mg_xNi_7$ intermetallics during soaking in alkaline medium for use as negative electrode in Ni-MH batteries

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One of the main issue with the use of renewable energies such as wind or solar energies is related to storage. In this field, the chemical or electrochemical use of hydrogen as an energy vector is promising and the nickel metal hydride (Ni-MH) batteries are of interest. Within the existing alloys M , $Y_{2-x}Mg_xNi_7$ are favorable materials to improve the specific capacity of the negative electrode. However, these alloys encounter corrosion issue, which prevent them up to now to replace the commercial ANi₅-based alloys (A: rare earth).

$Y_{2-x}Mg_xNi_7$ alloys with $0 \leq x \leq 0.5$ have been prepared then characterized by X-ray diffraction (XRD) and electron probe micro-analysis (EPMA). Their hydrogen absorption capacity was measured by the Sievert's method. The calendar corrosion of such alloys in alkaline medium was investigated by soaking powders from one day to several weeks in 8.7M KOH. Structural and elemental characterization techniques (XRD, electron microscopy) have been combined to identify the corrosion products developed at the interface of these alloys with potash. The influence of the magnesium on the corrosion products as well as on the corrosion rate will be discussed. The results will be compared to literature work on La-Ni-based materials [1, 2] and to previous work on the A_2Ni_7 (A=Y, Gd, and Sm) system [3, 4].

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ORAL O38:
**NEW BORANE-AMIDE BASED MATERIALS AS POTENTIAL SOLID-
STATE HYDROGEN STORAGE MATERIALS**

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In the beginning of the 2000s, a big interest has been given to ammonia borane (NH_3BH_3), in the field of solid-state hydrogen storage by the fact that it contains three hydridic hydrogens ($3 \text{H}^{\delta-}$) and three protic hydrogens ($3 \text{H}^{\delta+}$). It has high gravimetric hydrogen with 19.6 wt% H: this has attracted a flurry of recent investigations focusing on hydrogen release from it [1].

In this dynamic context, other nitrogen-containing boranes have been considered. One of these materials is hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$) prepared from sodium borohydride and hydrazine hemisulfate. Like ammonia borane, it has high gravimetric capacity hydrogen, with 15.4 wt%, owing to $4 \text{H}^{\delta+}$ and $3 \text{H}^{\delta-}$ [2]. Under heating, its dehydrogenation starts at 60°C , but high amounts of the unwanted and toxic hydrazine N_2H_4 are released. Alternatives have thus been searched for with the objective to propose materials that produces pure hydrogen.

The alkali hydrazinidoboranes ($\text{MN}_2\text{H}_3\text{BH}_3$) are indeed potential candidates for chemical hydrogen storage. When reacted with an alkali hydride MH ($\text{M} = \text{Li}, \text{Na}, \text{K}$), hydrazine borane transforms to such hydrazinidoborane derivative [3]. Another strategy is to make hydrazine borane react with an alkali amide. We have considered both approaches, the latter being the newer. Recently, we used the hydrogen-rich rich lithium amide LiNH_2 (8.7 wt% H) to make it react with the borane (ball-milling) and get a new material. The as-obtained samples were fully characterized. They were especially scrutinized by XRD while using tools dedicated to crystallography and to solve the structures.

The IDHEA 2016 meeting will thus be a great opportunity to present, for the first time, our results about the aforementioned novel material intended to be considered as potential solid-state chemical hydrogen storage material.

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HYDROGEN INTERACTION WITH PD-IR NANOALLOYS SUPPORTED ON CARBON: COMPOSITION AND SIZE EFFECT

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Bulk Pd-based alloys have been intensively studied since many years as possible candidates for hydrogen storage materials.[1] They are an excellent system to explore the alloying effect on the hydrogen sorption properties. Recently, nanosizing of metals is emerging as a promising route for the design of new materials for hydrogen storage.[2] However, one of the main issue of nanomaterials is the coalescence and the formation of large aggregates with bulk-like behavior. To stabilize nanosized metal particles against coalescence it is compulsory to use highly porous materials (carbons) as supports.

In this context, the present work reports on the nanosizing effects on the hydrogen sorption properties of Pd-Ir alloys. We have synthesized carbon supported Pd_{1-x}Ir_x nanoparticles with well controlled particle size (2-3.5 nm) by incipient wetness impregnation method followed by reduction (Figure 1a).

The binary phase diagrams of bulk Pd-Ir show both large miscibility gaps below 1480°C. Despite the miscibility gap, XRD and TEM investigations prove the formation of Pd-Ir nanoalloys over the whole chemical composition under our synthetic conditions. The hydrogen interaction with Pd-Ir nanoalloys strongly depends on their chemical composition and particle size. Pd-rich nanoalloys (up to 25 at.% Ir) absorb hydrogen whereas, Ir-rich (≥ 50 at.% Ir) nanoalloys do not absorb hydrogen at 1 bar and room temperature. Moreover, only Pd-rich nanoalloys with the large particle size (~ 3.5 nm) form a hydride phase under these conditions. The enthalpy of hydride formation is constant with the chemical composition, in contrast with the bulk Pd-Ir alloys that show a decrease with increasing Ir composition (Figure 1b). This proves clear size effects on the thermodynamic properties of nanoalloys.

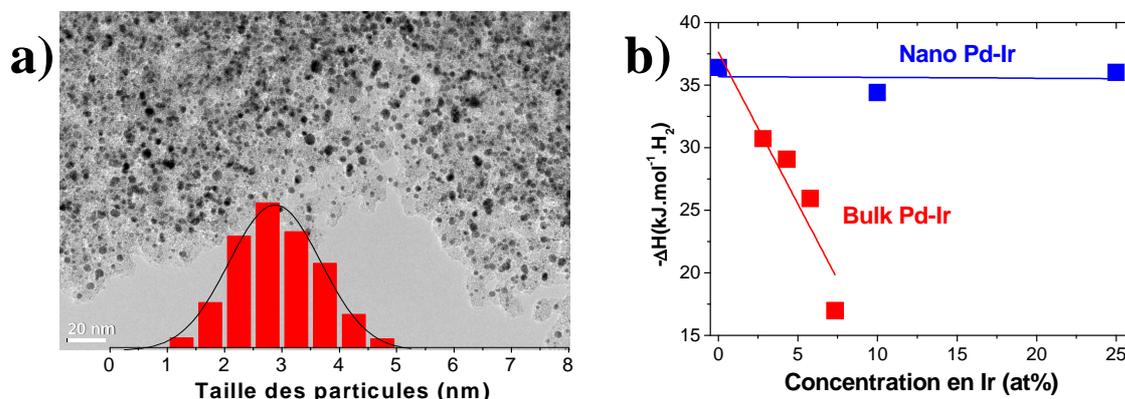


Figure 1: Typical TEM image of a Pd-Ir nanoalloy (Pd₅₀Ir₅₀) supported on carbon (a) and the evolution of the enthalpy of hydride formation for nano and bulk Pd-rich alloys (b).

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Experimental and modeling investigations on hydriding phenomena based on various charging scenarios

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Hydrogen solid storage in metallic hydrides still remains a hot topic which requires some upstream research. Our activities deal with the understanding of the behavior of the tank system including materials, heat exchanges and tank design, from the microscale to the macroscale. To do so, we developed, based on previous works [1, 2], a thermodynamic model allowing to simulate the response of a cylindrical tank according to different initial conditions, i.e. different charging scenarios. Main physical principles used in this description are: energy balance, mass balance, chemical equilibrium and apparent kinetics [3]. To complete this numerical tool, a dedicated bench test has been designed in order to extend experimental data acquisition such as the mass flow during absorption and desorption phases. Those data lead to improve comparison between experiments and simulations.

In the present work, several cases of hydrogen charging scenarios are investigated. The model allows predicting the response under following conditions: absorption under constant pressure, absorption under initial dosing pressure (Sievert method) and absorption under a constant inlet hydrogen flow, while effects of thermal regulation on the charging time are also discussed.

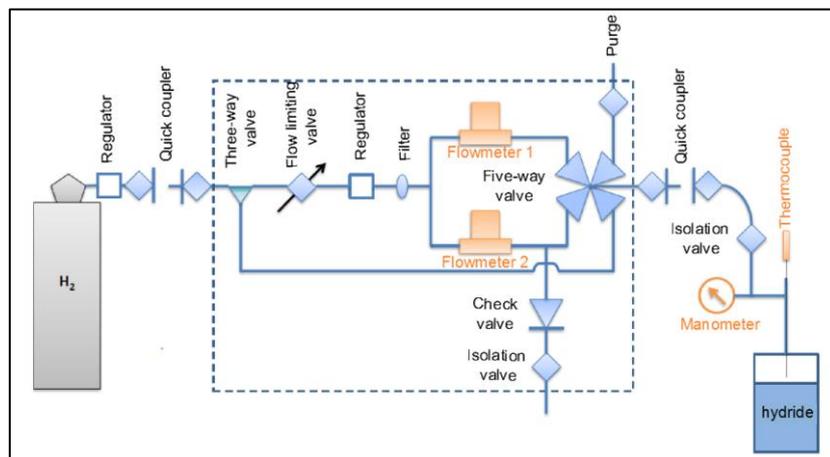


Figure 1: Detailed schematic of the developed bench test

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SIMULATION OF MECHANICAL STRENGTH OF HYDROGEN WOUND COMPOSITE PRESSURE VESSELS SUBJECTED TO FIRE

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Use of hydrogen energy at a large scale necessitates mastering the reliability of storage at very high pressure. Type-IV tanks are nowadays considered as a promising way. In order to better characterize the conditions that need to be achieved to avoid a failure of the composite pressure vessel in any accidental conditions, in particular fire, the FireComp project (a three year FCH JU funded pre-normative research project) aims to model the thermo-mechanical behavior of such high pressure storage. The main objective of FireComp project is to better characterize the conditions that need to be achieved to avoid burst. To this aim, reliable simulations of the thermo-mechanical behaviour of high pressure vessel made of composite material when exposed to fire conditions are necessary. They will allow, in the future, to improve current standards and fire protection strategies in order to protect people from both cylinder burst and hydrogen flame.

The risk analysis and the burst prediction of the storage tank in fire are key subjects. The first step in assessing the time a pressurized vessel can withstand fire without burst is the determination of the thermal / mechanical properties of the wound composite material the tank is made of, and the choice of the more convenient approach to model the composite degradation. The main difficulty, from the simulation point of view, is the coupling between the mechanical loading, temperature and fire aggression. The simulation of the tank behaviour cannot be conducted without a reliable thermo-mechanical behaviour model, which has to be simple enough to simulate large vessels. In this study, two different mechanical approaches have been selected and compared: a continuum damage mechanics approach and a basic, simple criterion approach. Besides the damage modelling, the FireComp project attempts to get over two difficulties: the thermomechanical coupling (in particular the consequence of the transformation of the composite material into char) and the challenging FE simulation of real type IV vessels, *i.e.*, structures containing a very large number of degrees of freedom.

The comparison of the simulation results with bonfire tests performed in the framework of FireComp are used to validate the modelling approaches and to identify their limits: a 36-liter vessel is subjected to an inner pressure of 700 bar and an incident flux supposed to be representative of a bon fire. Two experimental data are compared to the results of the simulations: the time to burst and the temperature measured by thermocouples put in the composite thickness. According to the performed bonfire tests, simulations at different inner pressure have been carried out. The themomechanical modelling is found to capture accurately the transition between a burst mode and a leak one: at lower pressurization levels, the liner has enough time to reach its melting point leading to vessel leak.

The research leading to these results has received funding from the European Union's Seventh Framework Program (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 325329.

This work pertains to the French Government program “Investissements d’Avenir” (LABEX INTERACTIFS, reference ANR-11-LABX-0017-01).

POSTER PO2:
**EXPERIMENTAL INVESTIGATION ON WATER TRANSFER IN
 PASSIVE TYPE PEFC MODULE**

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The fuel cells are clean and highly efficient energy conversion devices, which generate electricity from hydrogen and oxygen without emitting anything but water. Among them, PEFC, the polymer electrolyte fuel cell, is now increasingly being made into practical use because of its relatively low temperature operation and high power density capabilities. Most of the PEFCs now under research and development are referred to as stacks because of their stacked structure consisting of many cells and are aimed at automotive or domestic cogeneration system applications.

However, a fuel cell with a much simpler structure and capable of operating at nearly ambient temperature and pressure is suitable for small-sized generator sets for home and outdoor use. The passive type PEFC can operate under very low hydrogen pressure, taking in oxygen directly from the atmosphere. It needs neither a compressor to pressurize the supplied air nor a water cooling system for keeping the operating temperature around 80°C. It needs neither a humidifier nor a dehumidifier for hydrogen and air to maintain water management in the system. The simplified system configuration contributes to low failure probability and low manufacturing cost.

In this study, detailed experimental analyses were conducted with a passive type PEFC module consisting of 20 cells laid out in a plane as shown in Fig. 1. The passive type PEFC with the hydrogen circulating system using pressure difference has been proved to be effective for a long time operation, as it can avoid water plugging occurring in the hydrogen channels. Some properties were experimentally measured using the rated 55 W fuel cell module with the hydrogen circulating system during a constant current operation. The relationship between the properties, such as the output voltage of the fuel cell, the temperature of the module body and the temperature and humidity of hydrogen and air, was investigated. As a result, the water balance in the fuel cell module was clarified quantitatively as shown in Fig. 2 and the behavior of generated liquid water, which probably caused output voltage fluctuation, was discussed intensively.

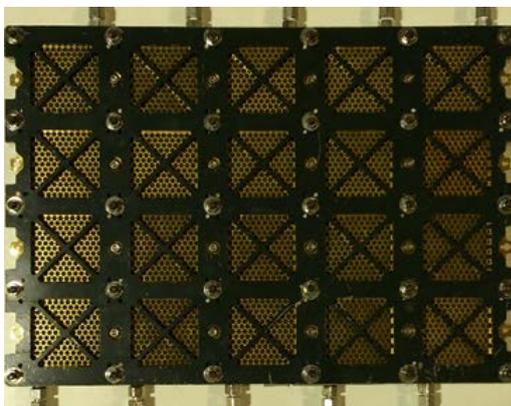


Fig. 1 Test fuel cell module

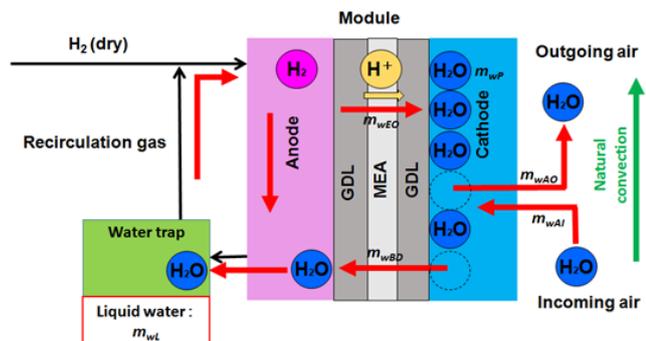


Fig. 2 Water balance in fuel cell module

POSTER PO3:
**MODELLING AND SIMULATION OF THE 46 KW PEM HIGH
PRESSURE WATER ELECTROLYZER INSTALLED ON THE
MYRTE PLATFORM**

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MYRTE, is a platform demonstrator composed by a photovoltaic array, a PEM fuel cell and a PEM water electrolyzer, both connected to three tanks of gas and water storages (H_2 , O_2 , and H_2O), a thermal management system and electricity converters associated with the different sub-systems. The principal aim of this platform is to study how hydrogen could be a good solution to store the energy associated to intermittent renewable energy source systems, such as photovoltaic array, for electrical grid application.

In this study, we present the modelling and simulation of the 46 kW PEM high pressure water electrolyzer installed on the MYRTE platform. An electrochemical steady-state and semi-empirical submodel coupled with a lumped thermal capacitance dynamic submodel was developed to predict the stack voltage and the system temperature evolution from the instantaneous operating conditions such as applied current, gas storage (H_2 and O_2) pressure tanks and the ambient temperature. The Particle Swarm Optimization algorithm was used to find the model parameter and a multivariable Matlab-Simulink® linked modular mathematical model was developed for validation. Results indicate that within a temperature range of 20-60°C, and within a pressure range of 15-35 bar, the stack voltage and the stack temperature evolution can be predicted even in transitory operating phases.

In the future, the developed Matlab-Simulink® model will integrate all the platform's component models and it will become a powerful tool to explore and to simulate new control strategies of the MYRTE platform.



MYRTE Platform, Ajaccio, France

Understanding ternary PEMFC nanocatalyst atomic arrangement during growth and annealing: a Molecular Dynamics approach.

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On one hand, Pt based ternary alloys are known to improve the activity and stability of PEMFC's catalysts. [1-2]. On the other hand, magnetron sputtering deposition has already demonstrated its ability for the fabrication of efficient PEMFC electrodes with high Pt utilization rate [3]. In the present study, MD simulations on $Pt_xM_yN_z$ (M; N, being less noble or common metals) deposition and growth are carried out for studying the preferred morphology and structure (size, geometry, atomic arrangements ...) of such clusters..

As the nanoparticle growth by sputtering methods is atomic by nature, simulations at the molecular level are expected to be relevant for understanding basic mechanisms of this deposition method. Indeed, molecular dynamics (MD) as being able to exactly calculating the trajectory of atomic systems is a suitable method for addressing this topic, especially in the context of plasma sputtering [4, 5]. Very recently, it has been shown that MD simulations allowed confirming and predicting the morphology and structure of Pt nanocatalysts [6,7] as well as for $Pt_xPd_yAu_z$ [8]. For the latter, a comparison is provided between sputtering and chemical synthesis methods.

Initial conditions of MD simulations are selected for matching experimental chemical and physical methods. Ternary catalyst $Pt_xPd_yAu_z$, $Pt_xNi_yAu_z$, $Pt_xCu_yAu_z$ and $Pt_xNi_yCu_z$ supported on porous carbon mimicking gas diffusion layers are studied. Radial distribution functions and X-Ray Diffraction pattern are systematically computed for enabling direct comparison with experiments.

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POSTER PO5

Characterization and modeling of commercially available High Temperature PBI-H₃PO₄ based MEAs in various operating conditions

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Commercially available High Temperature (HT) Membrane Electrode Assemblies (MEAs) using a phosphoric acid doped PolyBenzImidazole (PBI) membrane, from Advent Technologies Inc., were broke-in and then characterized in various conditions: oxygen and air as oxidant, gas stoichiometry (1.025 to 4) and gas flow rate control strategy. The main objective was to point out some particularities of HT-MEAs in comparison to Low Temperature Nafion based MEAs (LT-MEAs).

An Advent PBI HT MEA was tested in H₂/O₂ and H₂/air modes and polarization curves were measured including Electrochemical Impedance Spectroscopy (EIS) at specific currents. Modelling of the polarization curves shows that the activation losses appear to be significantly higher than those of LT-MEAs, probably due to the well-known adsorption of ion phosphate on platinum surface [1]. In contrast, losses due to mass-transfer processes seem to be significantly lower in HT-MEAs due to the absence of liquid water but not negligible due to the presence of phosphoric acid on the electrodes. Nyquist plots obtained with EIS measurements under air and oxygen show remarkably stable and reproducible impedance spectra compared to those of LT-MEAs (Fig. 1). This is probably due to the absence of liquid water, which can induce a quite unpredictable behaviour at low EIS frequencies (<1 Hz) with LT-MEAs. Furthermore, Nyquist plots obtained with oxygen are significantly different from those obtained with air, especially the low frequency arc. This arc is usually considered to be associated with mass-transfer processes or oscillations in gas channels [2]. In order to investigate the cause of this low frequency arc, two different gas flow rate control strategies were tested (Fig. 1). The first strategy was to maintain the gas flow at a constant value, which corresponded to the average sinusoidal EIS current. The second strategy consisted of adapting the gas flow rate in order to follow the sinusoidal current, which resulted in constant gas stoichiometry. Nyquist plots obtained with the second strategy show a positive imaginary arc at low frequencies (<400 mHz), which was not observed with the first strategy. This result suggests that the gas flow control strategy could significantly impact the low frequency arc and consequently complicates the physical interpretation of this arc.

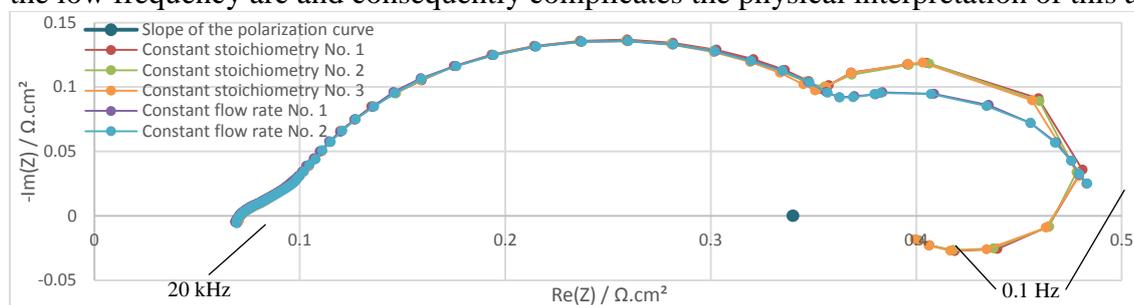


Fig. 1. Nyquist plots obtained by EIS measurements with different flow rate control strategies at 160°C and 0.2 A/cm² (apparent active surface area ≈ 45 cm²) in H₂/air mode.

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POSTER PO6:
**SAMARIA-DOPED CERIA/(Li,Na,K)CO₃ COMPOSITE AS POTENTIAL
ELECTROLYTES IN HYBRID FUEL CELL (350-450°C)**

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Composite materials based on oxide and molten salts are well-known to exhibit a high level of ionic conductivity at lower temperature (500-600°C) than Solid Oxide Fuel Cell operating one's (600-800°C) [1]. It has been clearly shown that the molten carbonate intrinsic properties in terms of conductivity level and melting temperature impact strongly the composite electrical behavior [2]. Thus in this work we've been studying the electrical behavior of Sm-doped ceria/(Li,Na,K)CO₃ taking benefit of the lower melting temperature of the ternary eutectic composition regarding the usual (Li,K)CO₃ and (Li,Na)CO₃ eutectics involved in Molten Carbonate Fuel Cells, i.e. 397°C compared to 488°C and 498°C respectively[3]. Measurements have been performed by impedance spectroscopy in dry air and H₂-based atmosphere, as a function of temperature. Composite stability is investigated during heating/cooling cycles. Thermal analyses such as TGA/DTA and GC (Gas Chromatography)-MS (Mass Spectrometry) coupling have been carried out as well as XRD, Raman and Infra-Red spectroscopies to get a deeper knowledge of these composite features. Khan et al already reported on this material in terms of ionic conductivity: 0.1 S.cm⁻¹ at 700°C [4]. In our study, as reported in Fig.1, this value is reached at 450°C after the carbonate melting yielding to a gain in conductivity of 300 times in the narrow temperature range 370-405°C. Furthermore, it is worth noting that the electrical behavior of SDC/(Li,Na,K)CO₃ composite is quite similar during both the cooling and the heating. This is quite promising as first requirements for a material in view of electrolyte application for oxide-based electrochemical cells.

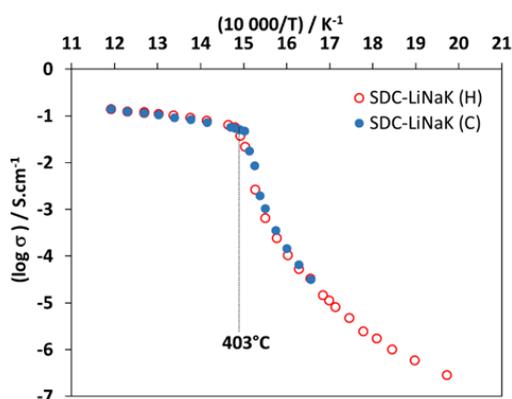


Figure 1: Arrhenius plot of Sm-doped ceria/(Li,Na,K)CO₃ composite conductivities during heating (H) and cooling (C) in dry air.

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POSTER P07:
**RESEARCH OF NEW ELECTROLYTE MATERIALS FOR SOLID
 OXIDE FUEL CELLS**

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Solid Oxide Fuel Cells operate at high temperature (above 800°C) as they are limited by the ionic conductivity of the electrolyte. This high temperature has some drawbacks, like the necessity to use energy to heat the cell before operation, the faster ageing of cell's components and a longer starting time.

Nowadays, most studies on electrolyte materials for Proton Ceramic Fuel Cell (PCFC or H⁺ SOFC) focus on substituted perovskite-type oxides based on BaCeO₃, which present an excellent H⁺ conductivity level of 0.01 S/cm at about 600°C. Zirconia-based electrolyte shows an equivalent O²⁻ conductivity level but at higher temperatures. Lowering the operating temperature of SOFC down to 500-600°C range should permit to limit reactivity between the different materials and reduce premature ageing of the cell components.

IMN is recognized internationally for its prospective work on new electrolytes for SOFC, among them, H⁺ electrolytes such as BaIn_{1-x}Ti_xO_{2.5+x/2} compounds showing 3 mS/cm for x values between 0.1 and 0.2 at 450°C [1], and the original lanthanum oxyborate La₂₆O₂₇(BO₃)₈. This later exhibits good protonic conductivity at 600°C [2] without any degradation of the mechanical properties of the ceramic through the hydration/dehydration process.

The work describes methods to discover new electrolyte materials for SOFC and first results of this study, with work on compounds like Ba₃Ti₃O₆(BO₃)₂ and K₃Sb₄O₁₀(BO₃)₃. These results will be discussed in detail.

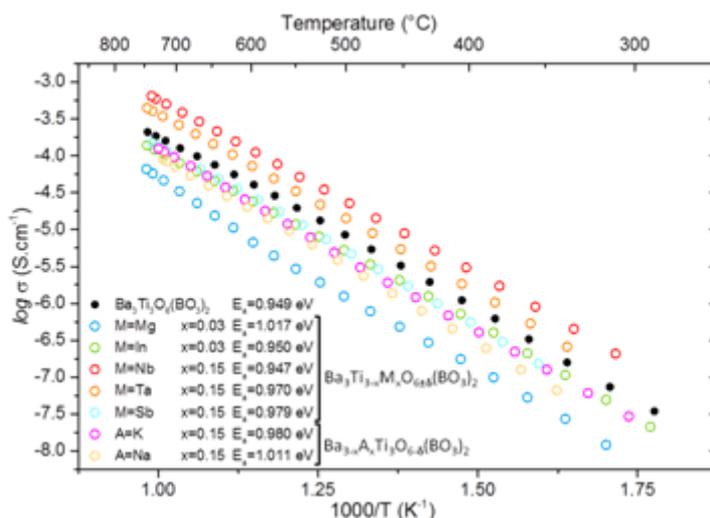


Figure 1: Ionic conductivity of eight prepared samples under dry air atmosphere.

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