MECHANICAL ENGINEERING | PHYSICS | PRESERVATION OF THE ARCHITECTURAL HERITAGE | STRUCTURAL, SEISMIC AND GEOTECHNICAL ENGINEERING | URBAN PLANNING, DESIGN AND POLICY | AEROSPACE ENGINEERING | ARCHITECTURAL COMPOSITION | ARCHITECTURE, BUILT ENVIRONMENT AND CONSTRUCTION ENGINEERING | ARCHITECTURAL, URBAN AND INTERIOR DESIGN | BIOENGINEERING | DESIGN | ELECTRICAL ENGINEERING | ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY | ENVIRONMENTAL AND INFRASTRUCTURE ENGINEERING | INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING | INFORMATION TECHNOLOGY | MANAGEMENT ENGINEERING | MATERIALS ENGINEERING | MATHEMATICAL MODELS AND METHODS IN ENGINEERING

PhD Yearbook | 2019

# DOCTORAL PROGRAM IN ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

Coordinator:
**Prof. Vincenzo Dossena**

The thesis works that are presented in this Yearbook are very representative of the multi-disciplinary research activity performed within the context of the PhD educational and research program in Energy and Nuclear Science and Technology (STEN). The latter is specifically designed to provide the student with the state-of-the-art in a wide range of research fields related to:

- production, conversion and transmission of energy
- rational use of energy
- nuclear systems, nuclear fuel cycle, radioprotection
- application of ionizing radiations
- methods for safety and reliability analysis
- development of innovative materials for energy applications

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# STUDY OF FUNDAMENTAL ASPECTS FOR THE APPLICATIONS OF OPEN CELLULAR STRUCTURES IN CATALYTIC PROCESSES

**Matteo Ambrosetti**

Supervisors : Prof. Gianpiero Groppi, Prof. Enrico Tronconi

Cellular structures (Open-cell Foams and Periodic Open Cellular Structures) are considered among the most promising candidates to be employed as enhanced substrates for catalytic reactors. These structures are characterized by high void fractions and specific surface areas which may grant low pressure drop and intensified fluid-to-solid heat and mass transfer rates. Besides, when using conductive materials, the totally interconnected solid matrix grants high effective heat conduction through the structure, strongly improving the global heat transfer performances of the catalyst supports. Many processes can take advantages of these features, either for the increase of the heat transfer performances that leads to the intensification of heat transfer-limited non-adiabatic processes or for the design of more compact gas-exhaust after-treatment devices thanks to the intensification of mass transfer rates. Despite their great potential, however, the application of these structures to industrial catalytic processes is limited by the lack of understanding of the related transport phenomena. The large deviations between the experimental data and the predictions of the available literature correlations for all the principal transport properties shows the needs for a detailed study of the most relevant transport phenomena in order to develop engineering correlations able to faithfully describe these quantities as a function of the operative conditions and the morphological features of the supports. This work aims at the fundamental analysis of the transport properties of open-cell foams and of Periodic Open Cellular Structures (POCS) coupling experimental studies with Computational Fluid Dynamics (CFD) simulations performed in the same research group to provide a cross-validation and a two-fold analysis of the investigated phenomena. The analysis of the simulation and of the experimental results requires adequate models for the foam morphological parameters, like e.g. specific surface area, characteristic lengths, that have been developed and are herein presented for open cell foams. The correlations herein developed can be employed for the design and optimizations of different processes and applications. Another fundamental aspect tackled in this research is the catalytic activation of these structures, that is a key issue for their application in real processes. Two different techniques are presented, namely electrodeposition on open cell foams – developed by Università di Bologna, and spin-coating, studied in cooperation with Mat4en lab of the Departement of Chemisty, Materials and Chemical Engineering "Giulio Natta", Polimi which was first adopted for open cell foams and then extended to the catalytic activation of POCS. These techniques were used for the preparation of samples that have been tested in the CO oxidation to assess the performances in reaction conditions. The studies described in this PhD project can be classified in four parts. In the first one the geometrical problems are addressed. In particular, a new geometrical model of open cell foams is developed, starting from few pieces of readily available geometrical information and adopting a fully theoretical approach. This model is able to provide an accurate estimation of the specific surface area and other quantities that are fundamental for the interpretation of simulations and tests. Based on this geometrical model, a virtual reconstruction procedure for open cell foams has been developed for the accurate computational (CFD) investigation of the transport properties in opencell foams. In the second part, investigations devoted to the description of coating techniques for open cell foams and POCS are described. Different activation methods for open cell foams withy high cell density – namely Dip Coating, Electro-deposition and Spin coating were compared by depositing a Pd/CeO2 catalyst on different structures for the CO oxidation. Spin coating resulted in the most promising methodology for the activation of these structures, since it enables the deposition of a uniform and adherent layer of catalyst, stable also under harsh reaction conditions – for example the strongly exothermal CO oxidation – see Figure 1. The analysis of mass and momentum transfer in foams and POCS was carried out, based on experimental data combined with CFD simulations. In particular experimental campaigns of CO oxidation in the diffusion-limited regime were performed on coated supports with different morphological properties in a wide range of fluid-dynamic conditions. Generalized correlations for the mass transfer in open cell foams and POCS have been derived for the accurate description of this phenomenon. Pressure drop tests have been performed on samples manufactured by 3D printing driven by the virtual geometrical reconstruction of open cell foams. Numerical simulations on the virtual models and experimental tests on the 3D printed samples are combined together to understand the effect of the porosity, cell size and strut shape on the pressure drop. These results have enabled the derivation of an engineering correlation and the comparison of these substrates to other conventional catalytic supports based on the trade-off between external mass transfer and pressure loss - see Figure 2. Finally in the fourth part a fundamental analysis of heat transfer across the connected solid matrix of open cell foams and POCS has been performed by dedicated experimental campaigns and numerical modeling activities. From an experimental standpoint, temperature profiles inside open cell foams in reactive and non-reactive conditions have been collected. To describe the temperature profiles in open cell foams, an original heterogeneous heat transfer model has been developed. This approach has enabled to evaluate effective heat transfer performances of these structures in view of their application in non-adiabatic catalytic processes, where the enhanced heat transfer properties allow for the effective reduction of the thermal gradients inside the reactor, thus enabling process intensification in strongly exo- or endo-thermal applications. The experimental activities carried out in this thesis work were carried out thanks to funding from MIUR–Project IFOAMS and ERC - Grant Agreement no. 694910 - INTENT.

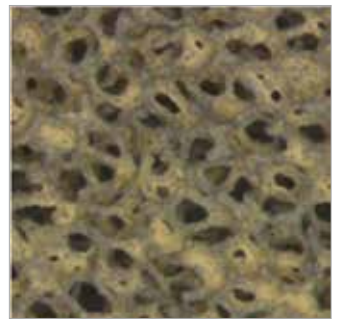

Fig. 1 - 100 PPI foam activated by spin coating with $Pd/CeO_2$

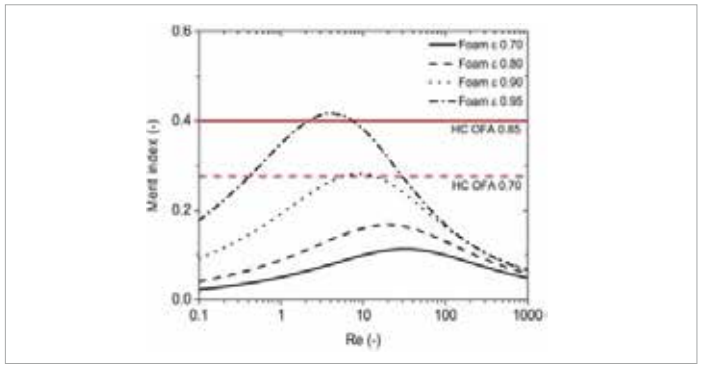


Fig. 2 - Tradeoff between mass transfer and pressure drops for open cell foams and square channel honeycombs

# INNOVATIVE METHODS FOR ON-LINE CONTROL-ORIENTED MODELING: AN APPLICATION ON THE TRIGA REACTOR

**Sara Boarin** - Supervisor: Prof. Antonio Cammi

This doctoral work develops an innovative approach to the control-oriented simulation, for application to nuclear reactor plant dynamics of current GEN-III and new GEN-IV. The TRIGA-MARK II in Pavia allowed model validation with experimental database.
The novelty consists in:
advancements in the characterization of the TRIGA physics and modeling;
new methods and approaches to the reactor plant dynamics prediction.

A non-linear model of the plant, with simplified geometry and spatial layout, is built with a twofold approach:
a-causal, declarative, in Dymola OOM simulation environment;
traditional, causal, in Matlab-Simulink environment.
Linear stability analysis is performed on the ODE system implemented in Simulink: stability regions are investigated by calculating the eigenvalues of the matrix of the dynamics, with respect to different values of fuel and moderator temperature reactivity coefficients.
The modeling scope includes the reactor pool, whose thermal inertia is key to the system dynamics, natural circulation across the core, cooling system and core reactivity:
fuel temperature coefficient is modeled with experimental fast power transient at different power values;
moderator temperature coefficient is modeled by elaborating results of previous research, based on Monte Carlo N-Particle transport code and thermal-hydraulic FEM COMSOL Multiphysics®;
Poison concentration dynamics is modeled and anti-reactivity has been calculated with experimental data. The whole model is validated with experimental transients performed by the candidate in March-May 2015, in collaboration with the INFN-Milano Bicocca.
The plant model simulation represents the best 'prior' knowledge of the system physics. This is nonetheless affected by simplifications and uncertainty due to incomplete understanding of the plant physics (e.g. friction factors, coolant flow regime, heat exchange model and parameters). This holds especially for innovative GEN-IV technology. On the other hand, the drawback of a control strategy based on measurement data alone is that measures come from few points in space and many relevant variables are not accessible by sensors (not observable). Measurements may be affected by noise or systematic error.

The control-oriented strategy proposed in this work is an innovative combination of the best available techniques to improve the accuracy of the dynamics prediction. It relies on the Kalman Filter (KF), an iterative prediction-correction algorithm that assimilates measures from the real system to improve 'prior' estimates.
If the relation between observables and state variables is given, the 'hidden' processes are predicted through an inverse problem technique.
KF is suitable for application to GEN-IV where harsh physical and chemical conditions limit the scope of use of sensors or their lifetime.
The Extended KF (EKF) is suitable for application to non-linear system dynamics and consists of a

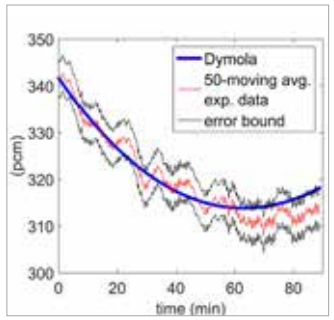


Fig.1 - Experimental transient: values of control rod reactivity. Dymola simulation, moving average of experimental values

dynamic linearization of the state space system and the application of the standard KF equations at each time step.
Convergence and consistency of the EKF are not granted, as for simple linear filter. Since EKF approximates the posterior probability $p(X_n|Z(0:n))$ as a Gaussian, it may have poor performance in some cases when the true posterior is heavily skewed or multimodal. EKF can be designed to produce good estimates of a non-linear system, provided that it is fine-tuned with suitable design parameters: the steady-state performance of the filter is uniquely determined by process noise covariance Q, observation noise covariance R and initial covariance matrix of the prediction error P(0). Unlike the case of linear filters, there is no general methodology for EKF parameters initialization; in complex system this task may become hard and critical.
This work adopts Particle Swarm Optimization (PSO) as a solution to the issue of EKF initialization. PSO is a stochastic optimization method where the position of a particle corresponds to a candidate solution of the optimization problem (i.e. a set of values for the EFK initialization). Particles move around the space testing new parameter values, to decrease the value of a properly defined object function. Their interactions result in iterative improvement of the quality of problem solutions over time, according to specific rules. PSO is faster than Genetic Algorithms and unlike evolutionary algorithms it does not use selection. The use of the PSO for the automatic tuning and initialization of the EKF is an advancement brought by this research work about the issue of EKF consistency and convergence. Results of EKF predictions show an accurate tracking of the process dynamics without overshooting or diverging. Stability and consistence are allowed by the PSO application to the EKF parameters initialization.
Some 2nd order effects on prediction accuracy may be further investigated or detailed:
the model is lumped parameter in some key elements (e.g. reactor pool);
true value of friction factor in core is unknown. Small variations can sensibly affect the mass flow rate in core and the neutron dynamics.
heat transfer model between fuel and coolant is averaged on the whole core.
reactivity feedback coefficient of fuel temperature is calculated by fitting experimental data, based on a model whose uncertainties are not 'closed' (according to the above mentioned issues).
Research developments may include:

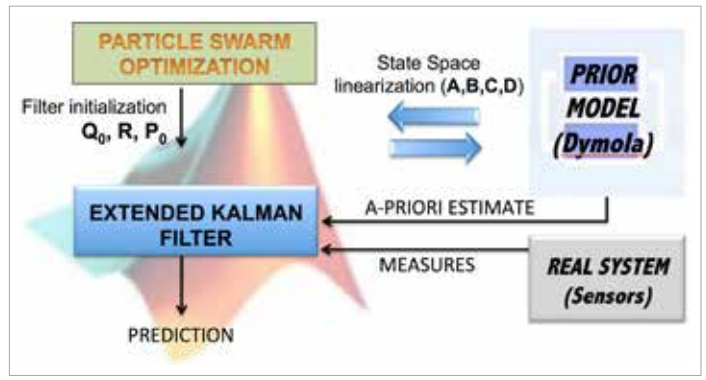


Fig. 2 - Conceptual scheme of the control-oriented simulation tool developed in this PhD research work

CFD simulation to provide insight on the flow regime and on the heat transfer conditions in the different core channels;
comparison with alternative prediction methods (e.g. Particle Filtering), in terms of prediction accuracy and computational effectiveness.
application of Reduced Order Methods, to further streamline the computational task, improving simulation accuracy and detail.
Bias introduced by systematic error in measurements is an open issue, which is not addressed by the EKF.

# DEVELOPMENT AND MODELLING OF A WATER-AMMONIA HEAT TRANSFORMER TO UPGRADE LOW-TEMPERATURE WASTE HEAT

**Silvia Garone** - Supervisor: Prof. Mario Motta
Tutor: Prof. Livio Mazzarella

In a growing energy demand scenario, exploiting industrial waste heat has relevant potential to improve the overall efficiency and reduce energy needs, emissions and costs. However, the main hurdle to waste heat use is often represented by its low temperature, making its integration in other processes challenging if not impossible without increasing the waste heat temperature.
Absorption heat transformers are one of the possible technologies to enhance waste heat recovery. They are thermal-driven devices to upgrade heat without the need of higher temperature sources or significant electricity consumptions. Indeed, their useful effect (raising the temperature level of a heat source) is brought about by degrading roughly half of the heat input itself and rejecting it to a cold heat sink.
In this way, the other half of the heat input is made available at higher temperature, making its exploitation easier. A particularly interesting application of this technology is to ease the integration of otherwise useless waste heat in district heating networks, as such an application could benefit from an optimal phasing between load and performances. In fact, both COP and heat duty of a heat transformer increase when a lower condensation temperature is available, as in colder days of peak heating demand.
This work focuses on such an application to improve very low-grade waste heat exploitation. Therefore, a heat transformer, able to recover heat at T<65°C and providing temperature lifts of ≈20K, has been developed and tested.
To work in such a low temperature field, up to now not investigated by experimental studies, water-ammonia was chosen as a working fluid. The choice of a pair well-known in the absorption field, but never used in heat transformers, is the novelty of the work, which has to deal with the issues related to the fact both species are volatile. For this reason, the research was carried out both experimentally and through thermodynamic simulation.
Major outcomes of this research are the achievement of a stably working prototype with good performances and the interpretation of the experimental results through a tuned model, able to give a full picture of all cycle parameters.
Assisted by thermodynamic simulation, testing was carried out on a small-scale prototype to define the most relevant hardware choices. In particular, designing an effective liquid-vapour separator was needed to manage the solution at restrictor outlet, normally with a high vapour quality. The geometry of the throttling valve and the solution charge were optimized, and a stably working prototype was obtained.
The final machine performances were characterized in an extensive experimental campaign, where both external and internal parameters were measured. Though heat duties and working range have a margin of improvement if pressure drops in the solution heat exchangers are limited, the performances (COP and Gross Temperature Lift) of the machine were quite in line with the expected values. Indeed, the experimental results seemed at least comparable with those of similar experimental studies, though carried out in different temperature ranges.
Nevertheless, the previously developed thermodynamic model, based upon assumptions commonly reported in literature, is not reliable in reproducing exactly the machine performances and trends. A new tuned model was developed, putting some of the assumptions into question and replacing them with empirical relations built upon the experimental data.
The resulting grey-box model, once validated, could provide more insight on non-measured variables such as concentrations and vapour quality. The main conclusion is that, despite the improvements in the liquid-vapour separator, which indeed allowed the cycle to work stably, a small amount of liquid solution is still dragged in the refrigerant circuit by the fast, two-phase flow at restrictor outlet, and this affects steady state performances as well as stability in off-design conditions.
As an alternative solution to improved separators, which would likely be extremely bulky and therefore scarcely suitable for industrial applications, the tuned model was used to study possible cycle improvements. In particular, an additional internal heat recovery could easily halve the vapour quality at restrictor outlet, making the flow easier to manage. The COP of the cycle is not expected to vary (apart from the improvements due to the expected refrigerant concentration increase), and some heat load would shift from the evaporator to the generator, a more complex exchanger (a falling film was used in the prototype). However, the study also showed that the theoretical advantage of using a falling film exchanger is not exploited in the real machine due to the separation issues. Replacing the falling film generator with a plate heat exchanger becomes a promising future development, which is expected to improve performances (especially if coupled with the aforementioned additional heat exchanger) thanks to the fact it normally contains a two-phase flow, while at the same time reducing weight and cost of the machine.
Finally, a possible alternative working fluid was examined, since many studies in literature claim that $NH_3$-$LiNO_3$ can ensure better performances than $NH_3$-$H_2O$, without the limitations of water-salts mixtures. However, thermodynamic simulations showed that, though ammonia lithium nitrate could theoretically achieve a better COP, heat transfer coefficients would be more or less halved as a consequence of the different thermos-physical properties (namely, higher viscosity), leading to the need of sensibly higher exchange areas. This is probably not a suitable solution for heat transformers, where investment cost is already a hindering factor and COP has a limited significance, since waste heat is used.

# FRICKE-BASED GEL FOR RADIATION THERAPY DOSIMETRY: CHARACTERIZATION AND APPLICABILITY

**Giulia Maria Liosi** - Supervisor: Prof. Francesca Celsa Giacobbo
Co-supervisor: prof. Mario Mariani

**Abstract**
Nowadays, an accurate and precise determination of the complete dose delivered to patients undergoing radiotherapy, i.e. the total dose to all organs from all sources of radiation treatment and imaging procedures necessary for planning and treatment verification, has acquired paramount importance. In particular, the increasing complexity of modern radiotherapy treatments has arisen the exigency to properly and accurately simulate the treatment plans in order to evaluate and minimize doses to healthy tissues and organs. Chemical gel dosimeters are promising tools to obtain experimental 3D measurement of the absorbed dose. In particular, this Ph.D. research project aims at investigating the Fricke gel dosimeters in order to attain a reproducible, accurate and sensitive tool for radiotherapy dosimetry applications. The final goal is the development of an optimized and standardized protocol, from preparation to analysis, for properly shaped phantoms to allow 3D pretreatment dosimetry. To this aim, a complete characterization and the study of the applicability for pre-treatment dosimetry were conducted.

**Introduction**
Fricke-based gel dosimeters are a class of chemical dosimeters composed of an acid solution of ferrous ions dispersed in a tissue equivalent gel matrix. This system relies on the dose dependent oxidation of ferrous ions into ferric ions. Thus, the ferric ions concentration is related to the total absorbed dose. The ferric ions concentration can be measured by means of both optical and MRI analysis.
The optical analysis exploits the different absorption properties of ferrous and ferric ions that absorb at about 250 nm and 304 nm respectively. A dye, the Xylenol Orange (XO), was added in order to shift the ferric ions absorption from UV to Vis range, so as to allow an easier optical analysis. This ligand forms complexes with the ferric ions that mainly absorb at about 585 nm. Thus, the difference in absorbance at 585 nm is linearly related to the ferric ions concentration, and consequently to the dose, by means of proper calibration factors. The slope of the calibration curve Abs (585 nm) vs Dose defines the sensitivity of the system. The linear dymanic range of the system is about 0 – 40 Gy, so that it can be used in most of the dosimetrical application of interest in medical fields. During the last decades, a great effort has been made to develop a three-dimensional optical analysis system.
Regarding the MRI analysis, the spin-lattice relaxation rate R1 quantifies the difference in ferrous and ferric ions concentration, and thus the dose. In fact, this technique exploits the different abilities of ferrous and ferric ions in enhancing relaxation of water protons. By means of proper T1-weighted acquisition sequences, a R1-map, and thus the dose map, can be obtained.
The imaging time is a fundamental parameter in order to avoid inaccuracy in the dose map evaluation due to ferrous ions auto-oxidation and ferric ions diffusion process. In fact, despite the presence of the gel matrix and ligand, several experimental campaigns have proven that the phenomenon of Fe3+ diffusion cannot be neglected and leads to a loss of the spatial information in few hours after irradiation, especially in case of deep dose gradient. This phenomenon has to be investigated and quantified in order to avoid data misinterpretation and inaccurate dose evaluation. In order to limit the diffusion process, several solutions were developed and tested in particular changing the system chemical compositions.
To conclude, gel dosimeters present several peculiarities that make them promising for several radiotherapy applications and in particular for modern dosimetrical challenges: 3D verification of complex treatments, small-fields, edge-of-field evaluation, skin dosimetry and so on. This Ph.D. project aims at investigation the open issues in order to obtain an accurate and sensitive tool to allow 3D pretreatment dosimetry.

**Experimental and Results**
The Fricke-based gel reference chemical compositions have been fully characterized in order to optimize and standardize a protocol from preparation to analysis, including a proper calibration procedure. In this step, small volume samples in form of standard spectrophotometer cuvette (4.5 mL) or layers (3 mm thickness) were employed. The preparation procedures for all the compositions tested were optimized in order to obtain a reproducible system. The dosimetrical properties, such as sensitivity, dose resolution and stability (both pre- and post-irradiation) were fully characterized by means of both UV-Vis and MRI technique. In particular, a complete characterization of the MRI parameters was conducted in order to obtain a satisfactory 3D dose mapping. As result, a protocol for small volume samples from preparation to analysis – both MRI and optical – was then fully developed and characterized. These results proved to be independent on the size of the samples employed.
The dosimetrical properties and the set protocol are than specific properties of the system. Therefore, a qualitative correlation to big phantom is allowed.
As explained, an accurate evaluation of the diffusion process is fundamental. Both UV-Vis and MRI techniques were tested to assess and compare the diffusion coefficients for all the studied systems. To this aim, standard use-protocols were developed in order to allow a fast and accurate comparison of different chemical compositions. Basic science studies were conducted in order to shine a light on the evidenced intrinsic system properties.
Firstly, the reference ligand, the XO, was fully characterized highlighting some issues correlated to impurities deriving from the synthesis as well as the Fe3+ complexation mechanism, which introduces optical artifacts in the UV-Vis analysis, reported in literature and not fully described. Furthermore, the role of the gel matrix in radical production was investigated in order to extensively understand the different dose response manifested by different gel dosimeters. For this purpose, a protocol for EPR analysis was designed, thus allowing a quick comparison of the radiolytical properties of gel matrices.
Innovative compositions were designed and tested in order to overcome the evidenced limits and issues. In particular, in order to overcome the issues of both ferric ions diffusion process and the limits previously highlighted for the reference ligand XO, a novel ligand was conceived and developed. A complete characterization of the dosimetrical properties of this new system was conducted to achieve a protocol from preparation to analysis, both optical and MRI.
The diffusion coefficient was then studied thanks to the previously optimized procedures exploiting gel layers. Finally, among the fully characterized systems, the optimal ones were chosen to be tested in specific applications. A proper phantom was developed to evaluate a SRS treatment plan, characterized by small fields. A complete protocol from preparation to MRI analysis was designed. The SRS treatment plan was developed on the CT images of the phantom. A 2D relative dosimetry was conducted with respect to a golden standard, a GafChromic film. Further investigations are still ongoing to obtained absolute 3D dosimetry. Finally, gel layers were designed to accurately measure low doses, in particular to evaluate the skin doses absorbed during breast treatment. A use-protocol for a fast calibration was designed to accurately measure doses down to 25cGy.

**Conclusions**
In conclusion, the results described in this Ph.D. thesis proved the effective applicability of the Frickebased gel dosimeters to modern challenges of pretreatment dosimetry. Moreover, fundamental data were obtained to better address the future researches concerning possible chemical modifications aimed at further improving the dosimetric performance and potentiality of the system.

# RADIATION-INDUCED EFFECTS ON POLYMERIC MATRICES FOR INDUSTRIAL, BIOMEDICAL AND ENVIRONMENTAL APPLICATIONS

**Maddalena Negrin** - Supervisors: Prof. Mario Mariani, Dr. Elena Macerata
Tutor: Prof. Francesca Giacobbo

Plastics have successfully penetrated the global market thanks to their simple and cost-effective processing along with outstanding properties, versatility, light weight, resistance to physical aging and biological attack. Most of the conventional petrochemical-based plastics are not biodegradable and the production of ecofriendly plastics, with high degree of degradability and bio-based, is still limited by the high production costs as well as by the poorer properties. The importance of enhancing the degradability of plastic recently gained attention due to the large amount of plastic waste that goes into the environment every year and damages environmental, animal and human health. It is well known that ionizing radiations affect polymer properties and they could potentially represent an efficient strategy to affect and enhance the compostability of plastic waste.
The radiation-assisted degradation pre-treatment could be employed in an innovative, eco-efficient biotechnological approach for safely disposing the growing amount of plastic wastes occurring in landfills, terrestrial and aquatic environments, thus contributing to improve the good environmental status of the planet.
The aim of the present PhD project is to investigate morphological and nano-structural changes induced by ionizing radiation on aliphatic polymers in order to evaluate if a radiation-based pretreatment could efficiently affect the biodegradability in compost. With the objective to draw general considerations, three polymeric systems were considered, with a different rate of biodegradation: *months*, *years* and *decades*. Newly synthesized polymers that fulfill sustainability criteria have been selected as biodegradable and slow- degrading systems that are random copolymers based on Poly(butylene succinate) (PBS) and Poly(propylene cyclohexane dicarboxylate) (PPCE), respectively. Both systems have good thermal and mechanical properties that allow them to be used as eco-friendly and sustainable packaging materials. Polyethylene has been selected as a conventional synthetic non-biodegradable polymer. Since polyethylene is economic and displays an excellent stability, it is the most used conventional non-biodegradable plastic that currently accumulates into the environment.
In order to understand the overall modifications of the systems under study and to favor degradation, different irradiation conditions, in term of absorbed dose and irradiation environments, have been considered: a more reactive oxygen atmosphere, which favors degradation by oxidation, and water or hydrogen peroxide solutions, which should strongly affect the polymer surface. The simplest irradiation configuration was considered to keep the process feasible in an industrial operating gamma facility. The effects of such radiation-based treatments on the polymer properties strictly connected to the biodegradability have been studied by means of different analytical techniques. Finally, focused composting tests have been performed.

**Results**

The investigations performed allow deducting some general observations. According to the polymer structure, different absorbed doses or irradiation environments could be required to efficiently affect the properties that influence biodegradation. Ionizing radiation can induce modifications of the chemical structure of the polymer by the creation of radicals and oxidation products. The degradation of the molecular weight appears to be enhanced when the structure of the polymer is characterized by the presence of functional groups (*i.e.* thiodiethylene). Investigations on the biodegradable system highlighted that the introduction of sulphur atoms efficiently increases the sensibility of the system towards radiation while the introduction of the cycloaliphatic unit, as in PPCE-based systems, enabled to obtain polymers with a higher radiation resistance. The increase of surface wettability thanks to the formation of new functional groups, even in the case of slow degrading polymers, is related to an enhanced degradability. The radiation induced modifications of the crystalline fraction seem not to produce a negative effect on biodegradability.
The compostability tests evidenced that the effects induced on the degradability depend on the system stability and on the absorbed dose. As long as the stability of the system is increased, changing the irradiation environment could become determinant to significantly enhance the degradation. Oxidative environments favor degradation, in particular oxygen atmosphere and hydrogen peroxide solutions. The treatment in water efficiently affects the polymer surface leading to a better enhancement of wettability. The biodegradable copolymers showed an increased degradability even at low absorbed doses. Interestingly, a relevant difference was observed in the experiments where PBS was irradiated in water rather than in air: while PBS irradiated in air at 100 kGy resulted to be more resistant than the pristine one, PBS irradiated in water at the same absorbed dose degraded faster (Figure 1). In the case of slow degrading system, irradiation in air at 200 kGy succeeded in enhancing the rate of degradation of the copolymer films: over the same incubation period, the weight loss is about 1% for the pristine samples but increases up to the 16% when irradiated at 200 kGy. In the case of HDPE films, irradiation in air and particularly in oxygen at 200 kGy highlights a beginning of the degradation process after 180 days in compost. Disintegration tests evidenced a variation of the biodegradation rate of the treated systems, more evident as the incubation period increases. Limited to the preliminary data acquired, irradiation under specific reactive conditions seems to be effective towards biodegradation also in the case of recalcitrant polymers.

**Conclusions**

The importance of enhancing the degradability of plastics recently gained attention due to the large amount of plastic waste that goes into the environment every year damaging environmental, animal and human health. The research work developed in the present Ph.D. project contributed to demonstrate that ionizing radiation could be a feasible potential tool to improve the biodegradability of slow-degrading plastics, environmentally-friendly and economically competitive. According to the structure of the polymer, irradiation by gamma radiation can efficiently provoke changes in those properties that strongly affect biodegradability.

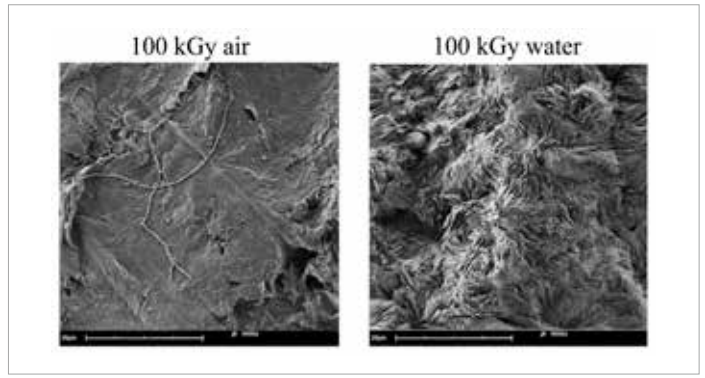


Fig. 1 - 1. SEM images of PBS irradiated at 100 kGy in air and water after 50 days in compost.

# NANOSTRUCTURED TITANIUM NITRIDE BY PULSED LASER DEPOSITION AS SUPPORT FOR FUEL CELL CATALYSTS

**Andrea Perego** - Tutor: Prof. Renzo Marchesi
Supervisors: Prof. Andrea Casalegno, Dr. Fabio Di Fonzo

Fuel cell technology is by now commercially available: it is mature enough to release on the market high power devices, efficient, reliable, and it can cover a wide range of application, from stationary generation to portable applications. Automotive is the most studied field, even though also the most challenging: the main drawback of hydrogen powered cars are is in fact the economical aspect. The high costs of production, as well as the limited durability make the fuel cells not convenient with respect to cheaper and more durable solutions (e.g. internal combustion engines, batteries).
Platinum-based catalysts, which to date are the state of the art materials for electrodes are too expensive and scarce, and the development of a hydrogen based economy will raise the demand even more. Moreover, the cheap and easy to process carbon support, another key component in high performance catalyst layers, suffer from corrosion at the typical potentials and pH of a fuel cell cathode. Research is moving towards developing new materials and new electrode architectures: a whole range of non-carbonaceous supports and various supports with high surface area are studied, to grant a high dispersion of the precious catalyst (and therefore less consumption) and stability in the harsh electrode environment. Among the various candidates studied to replace carbon, Titanium Nitride (TiN), has been elected as one of the most promising for its resistance to corrosion and metal-like conductivity, that make it suitable as an electrode material. On the other hand, this material is reported to be difficult to manufacture, and requires energy intensive processes. Thanks to the possibility to control the morphology of the films at the nanoscale, Pulsed Laser Deposition (PLD) is used in this work to manufacture a TiN nanostructured support that could be able to grant a good surface area for the catalyst, maintaining the characteristic stability of TiN.
Since no literature is available on such materials, the deposition conditions were chosen to obtain a morphology that can manage the trade-off between an open porous structure and a reasonable mechanical stability. The resulting film shows a peculiar tree-like, high aspect ratio structure material has a density of 0.88 g $cm^{-3}$ and an estimated BET area of 163 $m^2 g^{-1}$. (**Figure 1a**). XRD pattern reveals a nanocrystalline structure, given the low signal obtained from the measurements. Scherrer analysis show a mean crystalline domain size of 7-8 nm, while from calculations of the cell parameter a loss in the nitrogen content is observed. The reason lies in the PLD process: being nitrogen the most volatile specie involved, it tends to be depleted from the material during laser ablation. Raman spectroscopy confirms the nitrogen loss by showing increased vibrational modes generated by nitrogen vacancies. It also reveals a strong affinity of the material with oxygen and its propensity to oxidation. TEM analysis confirms the nanocrystalline nature of the material and highlights the presence of an amorphous matrix in which the nanocrystals are embedded (**Figure 1b**). EDS analysis, performed together with TEM reveals the presence of oxygen throughout the material. The native oxide layer that forms on the TiN surface is enhanced by the amorphous phase therefore a strong oxygen content is found in our nanostructures.
latinum has been deposited on the TiN nanotrees by means of pulsed electrodeposition. Pt is set to 0.3 mg $cm^{-2}$ using ICP spectroscopy to correlate the deposited charge with Pt loading. Pt clusters assemble into high aspect ratio lamellar structures on top of the TiN scaffold, probably due to the non-uniform electric field generated by its shape. ECSA is measured by cyclic voltammetry and is found to be around 32 $m^2 g^{-1}$ (**Figure 2a**). ORR performances are evaluated by linear sweep voltammetry. The current obtained at plateau are comparable with Pt/C E-TEK commercial catalyst, and the Tafel slope is as low as 68 mV $dec^{-1}$. On the other hand, the onset potential and half-wave potential are rather low, about 50 mV lower than the reference Pt/C. This could be the result of the combination of already mentioned surface oxidation and the amorphous phase that limits the electron transfer inside the structure.
Stability is also evaluated by means of specific U.S. DOE accelerated stress test protocols, aiming to evaluate the resistance to both platinum dissolution and support corrosion. With respect to the 40% target ECSA loss, platinum does not meet the requirements by only 4% difference, that can be overcome by optimizing the electrodeposition process and/or with different deposition method. On the other hand, the stability of the support is demonstrated with only a 7% ECSA loss after the specific AST. This proves that our catalyst is corrosion resistant in the harsh cell environment (**Figure 3a**). To test the PLD supports in a real fuel cell environment, a method to fabricate an actual MEA is proposed. Films coated with platinum deposited by ALD were transferred on a Nafion® 212 membrane and tested against a reference Pt/C anode (**Figure 3b**). The low proton conductivity of this configuration has been compensated with the introduction of liquid ionomer in the film by drop casting. Although the performances obtained are rather poor, as a reflection of the TiN scaffold's issues, good stability is also observed, with a 30% loss in the ECSA. The method to fabricate MEAs this way is proven to be solid, and could be a starting point for the further optimization of NSTF-based catalysts in a fuel cell environment, maintaining their characteristic structure otherwise lost during the fabrication of an ink.

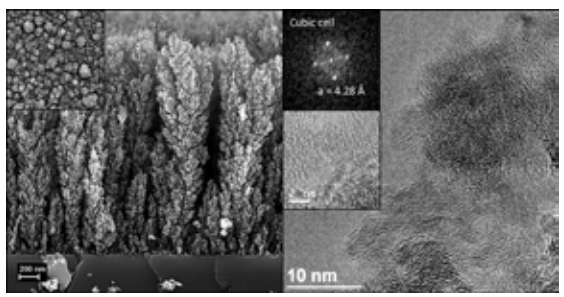


Fig. 1 -Left: Cross section and top view (inset) SEM images of the TiN nanostructured thin film. Right: HRTEM images of the TiN structure

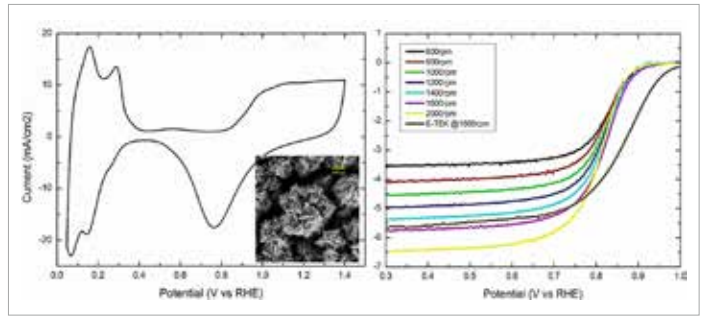


Fig. 1 - Left: Cyclic voltammetry of the TiN/Pt catalyst, scan rate was 150 mV/s Electrolyte was 0.5M $H_2SO_4$ solution. In the inset the top view SEM image. Right: ORR performance in RDE configuration in O2 saturated 0.5M $H_2SO_4$ solution

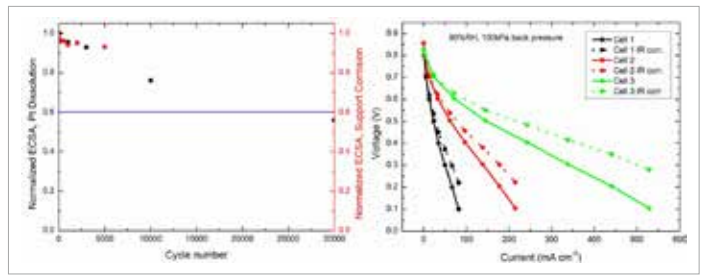


Fig. 3 - Left: results of the Pt dissolution and carbon corrosion stress tests, the blue line marks the DOE goal. Right: polarization curves of the MEAs at three different Nafion contents in the electrode: Cell 1 has none, Cell 2 has 0.5 mg/cm2 and Cell 3 has 0.1.

# PRESSURE DROP, HEAT TRANSFER AND FLOW PATTERN MAPS INSIDE SMOOTH AND ENHANCED TUBES DURING CONVECTIVE BOILING AND CONDENSATION OF R134A AND R1234ZE

**Phan Thanh Nhan** - Tutor: Prof. Luigi Pietro Maria Colombo
Advisor: Prof. Andrea Lucchini

Due to the increasing environmental concern the phase out of refrigerants commonly used in HVAC devices is taking place. Hence it is very important to find suitable fluids for the tomorrow HVAC systems. This thesis focuses on one of the banned fluids, which is widely used, the R134a and one of its possible alternatives. Among the new environmentally friendly fluids available as a replacement there are the hydro-fluoro-Olefin (HFO) R1234yf and R1234ze, which are characterized by a much smaller global warming potential (GWP) and much shorter atmospheric lifetime than R134a (table 1). The thesis aims to rate the performance of R134a and R1234ze and reports the experimental investigation concerning the heat transfer coefficient, the pressure drop and the flow pattern map during flow boiling and convective condensation inside microfin tube J60. As many enhanced tubes were developed in the past a benchmark is required to properly explain the results. It is common practice to compare a microfin tube with the smooth tube (figure 1 reports the geometrical features of the tubes) introducing some indexes related to the heat transfer area variation, the heat transfer coefficient variation and the pressure drop variation.

To properly analyze the fluids and the tubes, the experiments were performed in a wide range of operating conditions, which are unequivocally defined by four quantities: the saturation temperature $T_{sat}$, the mass flux G, the mean quality $x_m$ and the quality change $\Delta x$. During boiling the saturation temperature was $T_{sat}$=5°C while the other quantities intervals were: mass flux $G \in [67;333] kg/m^2s$, mean quality $x_m \in [0.15;0.95]$, quality change $\Delta x \in [0.05;0.4]$. For condensation, the saturation temperature was fixed at $T_{sat}$=35°C and the other quantities ranges were: mass flux $G \in [43;555] kg/m^2s$, mean quality $x_m \in [0.10;0.90]$, quality change $\Delta x \in [0.04;0.22]$. The collected data were post-processed and the results were grouped to highlight three main topics: the geometry effect (smooth tube versus micrfin tube J60, using R134a), the fluid effect (R134a versus R1234ze flowing inside microfin tube J60), the rating of the correlations for the heat transfer coefficient and the pressure drop.

The flow pattern analysis is the starting point to provide a correct interpretation of comparison between the microfin tube J60 and the smooth in terms of pressure drop and heat transfer coefficient. The main outcomes of the flow visualization lead to the following conclusions: the swirled microfins promote the annular flow, which onsets at lower mean quality and mass fluxes (figure 2), and shift the dryout to larger mean qualities (for the smooth tube it takes place in the range $x_m \in [0.80;0.90]$, while it was never observed during the experiments with the microfin tube). The main effect of the microfins is to keep the liquid in touch with the whole tube perimeter for a wider operating condition range. That explains the main advantage of the microfin tube: a larger heat transfer coefficient (larger than the area ratio). On the other hand its main drawback is a larger pressure drop. In the end it should be reported that, during some condensation experiments, the microfin tube J60 showed a lower heat transfer coefficient that the smooth tube. A possible explanation could be related to the too large number of fins and the flooding on the space between them which compromise the heat transfer performances.

The comparison between the fluids proved that the R1234ze is a very good replacement for R134a, as the post processing showed similar heat transfer coefficient and pressure drop in all the operating conditions.

The open literature provides a large number of correlations for the heat transfer coefficient and the pressure drop in microfin tubes. Their assessment is based on two parameters related to the experimental data, the mean percentage error and the standard deviation. According to the boiling experiments, for both fluids, the Han et al 2017 correlation seems to be the best option for the heat transfer coefficient while Kou et al 1996 and Choi et al 2001 correlations do the same for the pressure drop. For condensation, Cavallini et al 2009 correlation properly estimates the heat transfer coefficient for both the fluids. On the contrary, about pressure drop, is not available a correlation suitable for both fluids, the experiments highlighted that Goto et al 2001 correlation gives good results for R1234ze while Han et al 2005 correlation has the smallest percentage error but a large standard deviation. It should be concluded that further efforts are required to properly describe the fluid properties and the geometry characteristics of the microfin tubes.

| REFRIGERANT | TYPE | SAFETY | GWP | CRITICAL POINT | | MM | NORMAL BOILING POINT | LIFETIME |
|---|---|---|---|---|---|---|---|---|
| | | | | T[°C] | P [MPA] | [KG/KMOL] | [°C] | [DAY] |
| R134a | HFC | A1 | 1430 | 101 | 4.06 | 102 | -26.1 | 6862 |
| R1234yf | HFO | A2L | 4 | 95 | 3.38 | 114 | -29.5 | 11 |
| R1234ze | HFO | A2L | 6 | 110 | 3.64 | 114 | -19.0 | 16 |

Tab. 1 - Information of some Refrigerants

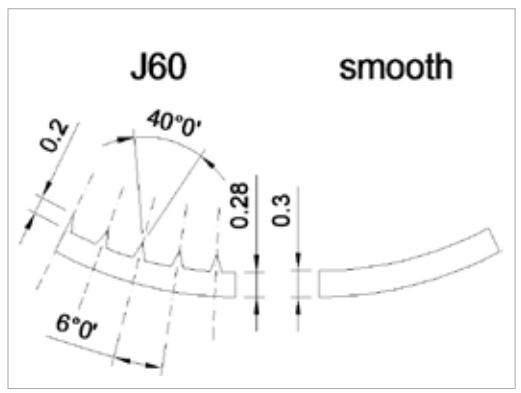


Fig. 1 - Geometry of smooth tube and microfin tube J60

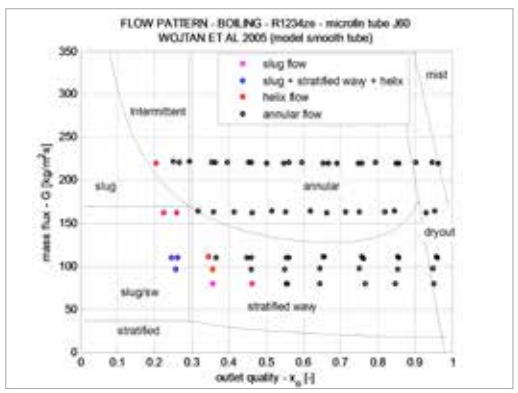


Fig. 2 - flow pattern from experiment of microfin tube J60

# MODELLING AND ASSESSMENT OF INERT GAS BEHAVIOUR IN $UO_2$ NUCLEAR FUEL FOR TRANSIENT ANALYSIS

**Davide Pizzocri**

Supervisors: Prof. Lelio Luzzi, Giovanni Pastore, Paul Van Uffelen

This thesis work concerns the modelling and the assessment of inert gas behaviour (IGB) in $UO_2$ nuclear fuel, with application to integral fuel performance codes (FPC) and emphasis on transient behaviour. The proper modelling of IGB during transients is fundamental for the performance (and safety) analysis of nuclear fuel rods, since IGB affects the thermo-mechanical condition of the fuel rods and can represent a limiting life factor for their permanence in reactor. In view of its crucial importance, IGB modelling is the main topic in several international projects. This thesis work is grafted in the FUMAC project, coordinated by the International Atomic Energy Agency (IAEA), the INSPYRE and COMBATFUEL H2020 Projects, supported by the European Commission, and the SciDAC Project on fission gas behaviour of the US DOE. For the sake of effectively and efficiently modelling IGB at the engineering scale, i.e., at the scale of FPCs (pellet and fuel rod level), it is fundamental to find a compromise between physical description of meso-scale processes concerning IGB (occurring at the scale of fuel grains) and the computational effort they impose to a fuel performance code. I adopted a modelling strategy mixed between physics-based and semi-empirical, always aiming at obtaining a conveniently simple description of IGB, suitable for FPCs. The considered IGB phenomena are:

- The evolution of the intra-granular bubble population, which can be responsible of up to half of the gaseous swelling during transients and strongly interacts with the diffusion of single gas atoms towards the grain boundaries.
- The burst release of gas occurring during temperature transients and ascribed to the micro-cracking of grain boundaries.
- The formation of the high burnup structure (HBS) with a combined description of the grain recrystallization and of the intra-granular gas depletion.

I proceeded by developing three IGB models, dedicated respectively to intra-granular, inter-granular and high burnup structure gas behaviour. Each of these models embodies peculiar physical phenomena (intra-granular bubble nucleation, intra-granular bubble coarsening, grain-boundary micro-cracking, HBS grain recrystallization) which all together allow for representing the complete evolution of inert gas behaviour during transients. This represents a significant step forward with respect to the state of art, in which some of these phenomena are represented by fully empirical correlations (with none or very limited transient capabilities) and others are completely not represented despite their potential impact on the fuel performance. I compared the results of each developed model with experimental data, according to a dedicated validation strategy (comprising uncertainty and sensitivity analyses), always showing an improvement with respect to available state-of-the-art models. In conjunction with this modelling activity, I developed two efficient numerical algorithms dedicated to the solution of specific partial differential equations (PDEs) with time-varying coefficients present in the model. In particular, the PolyPole-1 is developed for operational transients, whereas PolyPole-2 is developed for a system of PDEs overcoming quasi-stationary approaches currently used in FPCs, enabling a more representative simulation of fast transient conditions (e.g., during reactivity-initiated accidents, RIA). I verified the algorithms against a reference finite-difference algorithm in dedicated numerical experiments considering randomly generated transient histories, showing their accuracy and computational time in line with FPC requirements. Overall, the outcome of this thesis encompasses several different aspects in IGB modelling, i.e., both intra- and inter-granular behaviour, both regular fuel structure and HBS, both normal operating and transient conditions, both representation of physical phenomena and numerical aspects. All the models and the algorithms developed in this thesis have been implemented in FPCs. I personally performed the implementation in BISON (developed at Idaho National Laboratory, INL) and TRANSURANUS (developed at JRC-Karlsruhe), or directly collaborated with the code developers. Moreover, all the developed models and algorithms are available in the 0D stand-alone SCIANTIX code, developed as part of this thesis. SCIANTIX represents a POLIMI-owned software that can be included as an IGB module in existing FPCs, according to a multi-physics/multi-scale coupling strategy. In fact, in addition to providing a means for engineering calculations, thanks to their physical basis the models can be informed with parameters extracted at the smaller scales through atomistic calculations. Hence, the developed models provide an interface for scale bridging within multiscale modelling approaches. The new models are applicable with minor modifications to different fuel materials, since the main physical phenomena driving IGB are present in many fuel materials. The results shown are focused on $UO_2$, but extension to other materials is of future interest. For example, in the frame of a collaboration between POLIMI and INL, we are extending the present intra- and inter-granular models for application to uranium silicide fuels. Summarizing, the main outcomes of this PhD thesis are:

- The development and assessment of a physically-based IGB model (representing intra-granular, inter-granular and HBS IGB) suitable for transient analysis and applicable in FPCs. The development of numerical algorithms capable of solving the equations of the new model with computational requirements in line with FPCs.
- The development and verification of SCIANTIX, a 0D IGB code useful for testing, verification and validation of models and specifically designed for coupling with existing FPCs.
- The actual inclusion of the developed models and algorithms in FPCs, which represents a fundamental achievement from an engineering perspective.

The results obtained pave the way for further developments in several directions. A first direction is represented by the extension of the IGB model itself. As far as inert gas in oxide fuels is concerned, the extension of the work on helium is crucial (e.g., introducing in FPCs correlations for helium diffusivity and solubility in oxide fuel) due to the important role played by this gas in MOX fuels, at high burnup, and in storage conditions as well. More in general, are of sure interest the further development of the HBS model by including the HBS porosity description, the extension to other fuel materials (e.g., MOX, uranium silicide), the extension to include other non-inert fission products (e.g., caesium and iodine), the inclusion of the description of collateral physical phenomena (e.g., restructuring of MOX fuels in fast reactor conditions). Second fundamental direction is the continuation of the validation of fuel performance codes incorporating the new models against integral irradiation experiments (already performed for the inter-granular gas behaviour model). This will allow quantifying the improvement brought in using these new models. Code-to-code comparison will provide fundamental insights on code behaviour, pointing out further directions for code development. Moreover, more extensive validation is envisaged with SCIANTIX to further assess the developed models. Another fundamental direction for further research is represented by the optimization of SCIANTIX. This will lead to the development and licensing of a general tool for the development of new meso-scale models in the field of nuclear fuel performance, allowing for its use as a meso-scale IGB module in the framework of fuel performance codes.

# DMFC LOCAL PERFORMANCE INVESTIGATION FOR OPTIMIZED DURABILITY

**Claudio Rabissi** - Advisor: Prof. Andrea Casalegno

Undoubtedly, humankind development strictly bonds with energy technology progresses. Available, cheap and easy energy solutions are essentials feedings for global advance. In the last decades, unpreceded increasing mobility needs have been pushing energy technology towards novel solutions to meet an increasing demand for on-the-go power and energy availability. Both transportation sector, relying for around 90% on fossil fuel powered internal combustion engines (ICEs), and electronics, mostly Li-ION battery technology based, are eager of new, groundbreaking, solutions. Recently increasing global concerns for environmental compatibility, together with the awareness of them being a finite resource, fraught with geopolitical constraints and increasing costs of extraction, are strongly pushing beyond this two-century period of absolute dependence on fossil fuels. On the other side, unstoppable increasing power demands of portable electronic applications are not being met by batteries technology improvements, developing the so-called "run time gap" and growing safety issues still to be addressed. In this scenario, among potential long-term solutions, fuel cells based on potentially renewable fuels have received considerable attention. In the transportation field, polymer electrolyte membrane fuel cells (PEMFCs) can extract significantly more power out of the same quantity of fuel when compared to traditional ICEs, thereby providing 30–90% higher efficiency (on a "well-to-wheels" basis), with absolute no environmental issues. Despite on-board storage constraints, lack of widely-developed $H_2$ distribution infrastructure, durability and cost issues, the commercialization of $H_2$-powered PEMFC vehicles has already started. Among PEMFC technologies, immediate application of liquid-fed direct methanol fuel cell (DMFC) technology to the transportation sector is impeded by the daunting cost, limited durability and power-density issues. DMFC is more considered for markets as micro to small portable power applications, where the shorter product lifetimes and the much higher price have a lower relative importance. Actually, commercial application for DMFC technology move from micro electronics up to small industrial vehicular and portable powering applications, where long range and very short recharge times are key features, ranging from mW up to several kW of installed power per application. Thanks to research efforts, knowledge has much improved in various fields such as catalysis, electrolytes, electrode structures, theoretical understanding of the processes and fuel cell engineering, resulting in an initial performance of DMFC nowadays acceptable for practical applications, despite several drawbacks of the technology. Unfortunately, durability and cost still remain challenging issues. It is relatively well documented that in DMFC (even more than PEMFC) performance is the result of a complex interaction of many design, assembling and operating parameters as well as by the properties and microstructure of materials used on their construction, which are locally varying. The most important implication is an uneven electrochemical response over MEA active area, that may lead to low reactants and electrocatalyst utilization, reducing the overall efficiency and accelerating (uneven) aging of components. Typically, literature's most diffused approach about DMFC inhomogeneous fading is to separately discuss performance distribution and uneven aging of components. While the former is investigated by means of highly locally resolved hardware, the latter relies on local post-mortem analysis, seldom correlating the results to identify determining mechanisms. Moreover, few attempts of actual optimization are present, revealing a gap between investigation and improvements development. In this frame, the present work proposes a chronological and conceptual path starting from literature review on the field, passing through the methodology development, crossing experimental and modeling investigation, to finally lead to developing optimizations of the MEA critical components, concluding with improvement demonstration on a commercial meaningful setup. A locally resolved experimental methodology has been appositely developed (depicted in Fig.1), combining novel RHE setup together with a macro-Segmented fuel cell hardware, permitting to spatially map electrodes potential, current density and impedance. Also, previously developed modelling platform has been properly improved to describe local performance and water distribution effects. Investigation of local performance and degradation revealed that water distribution and heterogeneously cycling cathode potential have a strong influence on active layers' current density redistribution over time and local degradation. A novel cathode electrode, based on highly graphitized carbon support, has been selected demonstrating an increased stability under flooded conditions, leading to homogeneous material degradation. However, being local performance fading still unevenly driven by local operating limitations, cathode catalyst layer component have been locally improved through modelling optimization to ensure locally optimized operation. This lead to an in-plane gradient catalyst and ionomer loading for cathode electrode, that revealed a strong impact on local performance distribution, controllable by means of operating parameters. As depicted in fig.2, from a comparison of 500 h degradation test, performed by means of electrochemical diagnostics together with TEM and XPS post-mortem analyses, the improved MEA demonstrated 70% lower degradation rate than the reference MEA, revealing more homogeneous operation and fading. The results reveal a large scope for improvement obtainable pursuing a locally optimized operation and may enable improvement in overall technology development. For this reasons, the promising methodology has been finally demonstrated on a commercial-meaningful device and filed in a PCT patent.

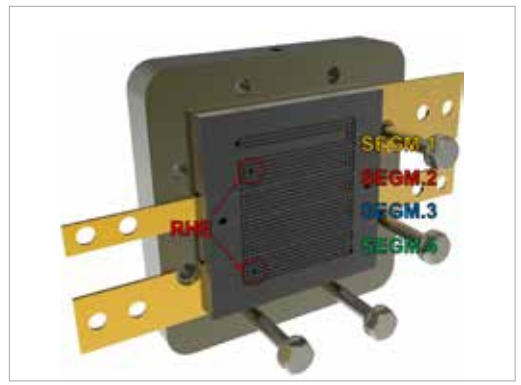


Fig. 1 - Rendering of macro-Segmented Fuel Cell (m-SFC) hardware, featuring segmentation in to 4 macro-regions and local mass-sampling/RHE predisposition

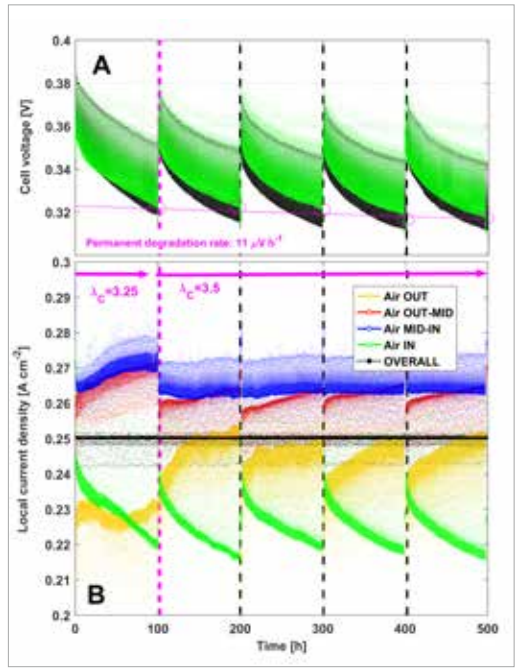


Fig. 2 - Cell voltage (A) decay comparison between base MEA (black) and improved MEA (green) together with local current density (B) evolution, during a 500 h discontinuous reference degradation test performed at 0.25 A cm-2. Purple dotted line indicates operating parameter adjustment.

# MODELLING ENDOGENOUS COMPLEXITIES IN RURAL ELECTRIFICATION: ON THE LOCAL DYNAMICS OF GROWTH AND THE PLANNING OF OFF-GRID SYSTEMS

**Fabio Riva -** Supervisor: Prof. Emanuela Colombo
Co-supervisor: Prof. Marco Merlo - Tutor: Prof. Andrea Casalegno

According to the Agenda 2030 launched by the United Nations in 2015, *to ensure access to affordable, reliable, sustainable, and modern energy for all* is now recognised as a fundamental goal to reach by 2030. Focusing on electrification, it is estimated that 2.6 billion people will have to be electrified by 2030 to ensure universal access to electricity, highlighting the need and the urgency to develop sustainable and appropriate approaches to electricity planning. According to this, the thesis deals with methods, approaches, and models for formulating and designing sustainable long-term electrification plans for rural off-grid areas of the world. In particular, the scientific literature highlights the lack of appropriate modelling frameworks for assessing, projecting, and integrating the electricity demand within the rural energy planning endeavour. It also reveals a weak understanding of the dynamic and multifaceted complexities that involve electricity access and socio-economic development.

To fill these gaps, the thesis sets a novel starting point for the research work on energy demand models and their integration in electrification planning procedures, by setting the following three specific objectives:

1) *To investigate and discuss the challenge of electricity demand assessment and modelling for rural electrification*. This objective is pursued through the development and analysis of specific case-studies, an extensive synthesis and capitalisation of the related scientific literature, and the characterisation of the main modelling fundamentals of this research field. The relevance of electricity demand in rural electricity planning is introduced, by discussing and demonstrating that unreliable forecasts and projections of short- and long-term electricity demand can negatively impact the techno-economic sizing of off-grid power systems. This implies a raising awareness on the criticality of electricity load assessment in rural electrification planning and advocates more research on this topic. The current methodologies adopted for projecting long-term energy demand along the planning horizon are then evaluated, finding that most of the rural energy planning literature neglects the aspect of long-term evaluation of electricity demand. It is also found that modelling long-term projections of energy demand needs to consider the multifaceted aspects related to it, which have both a technical and a socio-economic nature. This leads to the development of the main important causal loop diagrams that characterise the technical and socio-economic dimensions of the electricity-development nexus (Figure 1), proving that the evolution of rural electricity demand can be explained by endogenous dynamics. This result advocates the promotion of modelling techniques able to frame, understand, discuss, and quantitatively formulate the behaviour of complex systems, such as System Dynamics.
2) *To assess and model the fundamental dynamics, variables, and exogenous policies that characterise the electricity-development nexus and determine the evolution of electricity demand.* The chosen method to achieve this objective is System Dynamics. All the steps are based on a real case-study as reference, i.e. a hydroelectric-based electrification programme implemented in the rural community of Ikondo, Tanzania, in 2005 by the Italian NGO named CEFA Onlus. The *conceptualisation* of the model leads to the analysis of the dynamic problem to solve and the purpose to achieve, the model boundary and key variables, and their behaviour. The *formulation* phase results in the development of a novel simulation model – based on Vensim DSS ® – which simulates the impact of electricity access and use on the socio-economic development experienced in Ikondo, and the related feedback on the community's electricity consumption. This result provides the first important goal in the research and modelling work committed to develop more general, flexible, and customizable energy demand models. The *calibration* of the model and the analysis of the uncertainties through the Markov-chain Monte-Carlo (MCMC) contributes to build confidence in the model structure by verifying its ability to replicate the observed historical behaviour of the system, and by uncovering model flaws and hidden dynamics. The calibration also confirms the appropriateness of system dynamics in modelling the complexities behind the evolution of rural electricity demand, and it provides new modelling insights on some presumed dynamics and their impact on the electricity-development nexus. The *testing* of the model leads to a novel assessment of the most relevant dynamics and it provides a novel discussion on model results when its inputs take on different values, until the extreme ones, and as if the model were tested for different contexts than Ikondo. Policy testing is also performed for exploring model behaviour when subjected to different polices and exogenous decision-making processes. It provides a list of complementary activities to couple with electrification programmes for enhancing their positive impact on rural communities. These results can support the definition of useful guidelines and best practices for rural electrification, and they advocate an updating of the traditional monitoring and evaluation frameworks commonly used for assessing energy access projects.
3) *To integrate demand, load, and energy optimisation models in a more comprehensive electricity planning procedure*. This is pursued by developing a computational soft-link between the system dynamics model, a stochastic load profiles generator, and a heuristic energy optimisation tool – implemented in Matlab. The result is a more comprehensive modelling framework for investigating electrification processes – if compared with the traditional approaches and hypotheses commonly adopted to assess and integrate electricity demand in rural electricity planning –, and it provides an important contribution towards the employment of the robust multi-year energy optimisation as the referring standard for off-grid electricity planning.

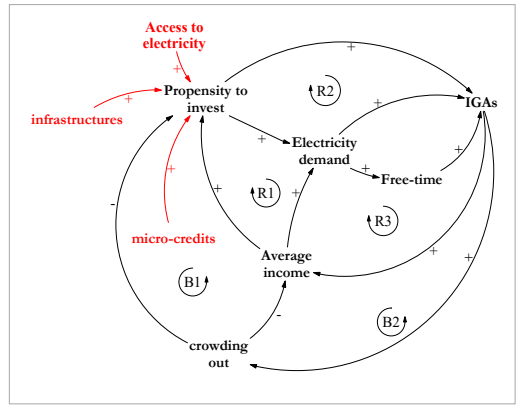


Fig. 1 - T Simplified causal-loop diagram representing the nexus between electricity use and the creation of rural income generating activities (IGAs).

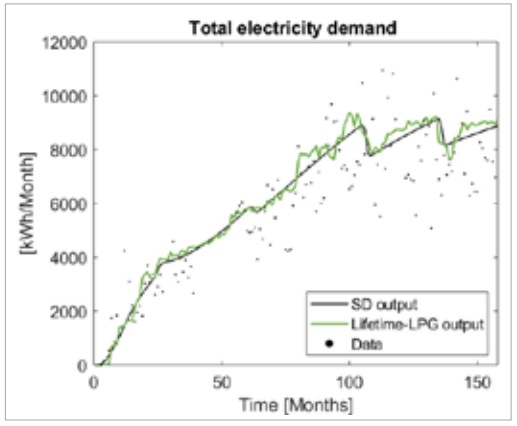


Fig.2 -Total electricity demand for the Ikondo village: measured data (black dots), simulated through System-Dynamics (black line), and simulated though the integration with system-dynamics and a stochastic load profiles generator (green line).

# A STUDY ON SUBMERGED SMALL MODULAR REACTORS: INTEGRAL DESIGN, PASSIVE SAFETY STRATEGY AND CRITICAL ISSUES

**Marco Santinello** - Advisor: prof. Marco Ricotti

The theme of the thesis work concerns the investigation of an underwater Small Modular Reactor (SMR). This concept potentially offers unique safety features in terms of enhanced protection towards Fukushima-like accident scenarios, i.e. loss of off-site power and loss of ultimate heat sink, loss of coolant accident and external events. The reference concept is Flexblue (Figure 1), a 160 $MW_{el}$ transportable and sub-sea based nuclear power unit developed by French company DCNS (now Naval Group). The plant adopts pressurized water technology and its safety relies on a passive system strategy. This concept is currently observed with interest by the nuclear community because of its innovative safety and security potentialities. The research developed during the three years of the PhD activity represents a proposal and a critical, albeit non-exhaustive, analysis of the reactor design and the potential safety features of a submerged SMR.
The outcomes of the thesis can be summarized with the following key-points.

a) The submerged SMR owns safety features that inherently protect from some of the most challenging accident scenarios. The safety strategy can rely on the presence of a heat sink, i.e. the water surrounding the reactor containment, which is permanent and infinite if the reactor is immersed into the sea or in an artificial lake. The development and deployment of this concept will represent a sort of "ultimate" solution to Fukushima-like scenarios.
b) The reactor to be placed inside the submerged containment must satisfy the constraint given by the limited hull diameter
c) and the heat transfer capability to the external water. To exploit the potentialities of the submerged concept, the reactor design must be appropriate for a fully passive safety strategy. The analysis of three proposed alternatives, i.e. VVER-type, SCOR-F and IRIS-like, has identified in the IRIS technology the most suitable design to gain compactness and to implement passive safety. A preliminary configuration has been proposed: it is a scaled version of IRIS with roughly half thermal output, where the design of primary components has been revisited to reduce the total height below 14 m.
d) A fully passive safety strategy for emergency reactor cooling has been identified, exploiting the external water as infinite heat sink. It is based on two reference processes for decay heat removal (Figure 2): (i) the natural circulation in the emergency heat removal system, if the primary circuit is intact; (ii) the long-term sump natural convection through the submerged containment, in case of a break in the primary circuit. This second process represents the ultimate solution for decay heat removal in case of failure of all the other safety systems.
e) The simulation of a station black-out scenario (intact primary circuit) and long-term cooling following a loss of coolant accident (broken primary circuit) has provided positive outcomes, predicting successful and effective decay heat removal in all the cases simulated. Simulations performed with the system code Relap5-Mod.3.3 have shown that well-designed passive system can ensure an unlimited grace period without the need of electrical inputs or human intervention.
f) A benchmark with the commercial system code Apros, developed by VTT Technical Research Center of Finland, on the long-term cooling scenario has shown the same positive outcome about the effectiveness of the sump natural circulation. However, the behavior of the flow resolved by Apros is remarkably different from the Relap5 case. The analysis has provided useful elements to understand the differences at the basis of the two system codes. In particular, the preliminary investigation on a two-phase flow test case has revealed that Apros tends to overestimate the two-phase heat transfer coefficient, with respect to Relap5 and empirical correlations. This outcome seemed quite odd and has stimulated VTT to improve the two-phase modeling structure of Apros 6 code, fixing some issues in the HTC calculation. An experimental testing is fundamental to assess the working principle of passive safety systems and to fill the gap of knowledge about several complex thermal-hydraulic phenomena. Two facilities have been designed in the framework of a proposal, namely INSPIRE, for the H2020 Euratom call on SMRs. The testing regards both the emergency heat Removal system and the heat transfer through the submerged containment. In addition, another experimental activity concerning an alternative configuration for the steam generator, i.e., the bayonet tube, is described.
g) Besides safety capabilities, the most relevant criticalities for the deployment of submerged SMRs have been identified and briefly discussed. The issues include (i) design of boron-free core, (ii) remote operation & control, (iii) maintenance and refueling, (iv) seismic assessment, (v) licensing procedures, (vi) international regulation, (vii) economic sustainability, (viii) public acceptance.

The findings of the thesis work about decay heat removal potentialities are very interesting and encourage further investigations to continue the development of the submerged SMR concept. The submerged concept could represent a "European" SMR proposal, in competition with US, Russian and Chinese designs. Future developments should be conducted in the framework of EU collaborations. Passive safety is a very strong point, whose benefits justify addressing the critical issues identified in the thesis. Joint efforts among industry, research centers/universities and regulatory bodies are fundamental to define the final design and achieve a valid European technology that is competitive in the global nuclear market.


Fig. 1 - Conceptual view of Flexblue power unit

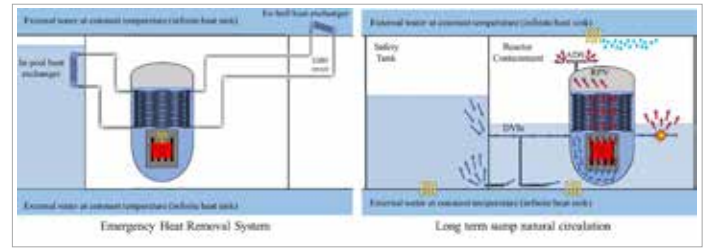


Fig.2 -Reference scenarios of the passive safety strategy

# DEVELOPMENT OF A COMPREHENSIVE CFD MODEL FOR SPARK-IGNITION ENGINE COMBUSTION

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Objective of this work is the development of a Comprehensive CFD Model to predict Spark-Ignition (SI) engine combustion. To this end, a run-time coupled Eulerian-Lagrangian strategy was chosen to describe ignition and flame propagation, accounting for complex electrical circuit features, stretch effects and thermo-diffusive flame instabilities (Lewis number influence). In particular, the effects of energy transfer from electrical circuit and turbulent flame propagation were fully decoupled. The first ones are taken into account by Lagrangian particles whose main purpose is to generate an initial burned field in the computational domain. Turbulent flame development is instead considered only in the Eulerian gas phase for a better description of the local flow effects. Concerning the turbulent combustion modelling, two different approaches were investigated. The Flame Surface Density model was used to validate the Comprehensive Model in a RANS context. The Artificially Thickened Flame (ATF) model was analyzed for future LES investigations and improved in terms of flame front detection and treatment of the mixture fraction gradient thickening. For what concerns the Comprehensive Model validation, several steps were followed. A preliminary assessment of proposed flame stretch and electrical circuit models was performed over simplified configurations, in order to understand separately their predicting capabilities. Then, experiments carried out at Michigan Tech University in a pressurized, constant-volume vessel were used to validate the general approach. On the other hand, the Darmstadt Turbulent Stratified Flame (TSF) burner was selected to provide a preliminary assessment of the ATF model implementation, because characterized by a three-pipes ejector where a stationary flame is generated over a lean-lean charge stratification. The final part of the work is dedicated to some first steps towards additional validations of the proposed modelling strategies. First, an heat losses analysis was carried out on the TSF burner, in preparation to future non-adiabatic investigations. Then, combustion tests were performed on the Orleans spherical constant-volume vessel, in which a nearly isotropic turbulence intensity can be controlled nearby the central ignition zone.

# A MODELING AND SIMULATION FRAMEWORK FOR ANALYZING FAILURES IN CYBER-PHYSICAL SYSTEMS FOR ENERGY APPLICATIONS

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Cyber-Physical Systems (CPSs) feature a tight combination of (and coordination between) the system computational units and physical elements. In particular, the integration of cyber resources into energy production processes enables real-time monitoring and dynamic control, during normal operation and accident conditions. CPSs are inevitably subjected to failures due to degradation and failure of the physical components, and to intentional or accidental breaches in the cyber units. Thus, risk assessment of CPSs must address both safety and security issues, because not only failures of hardware and software can cause damages and harms, but also cyber attacks can breach the CPS security and lead to serious consequences. Safety concerns (stochastic) components failures that can result in accidental scenarios leading the system towards unacceptable consequences. Security concerns malicious and intentional attacks that can impair both the physical and cyber parts of the system, and lead to unacceptable consequences.

In this PhD work, a general modeling and simulation framework has been developed for the failure analysis of CPSs, which include: I. identification and prioritization of hazards and threats (to identify the conditions that trigger anomalies in the systems and their causes), II. failure scenarios modeling and simulation (to characterize the system behavior under different operational conditions, including hazardous and malicious ones), III. consequence analysis (to explore the effects of stochastic component failures and cyber attacks onto the CPS functionality) and IV. protection design (to take decisions on recovery measures for increasing system resilience).

The proposed framework is fundamental to address all possible hazards and threats in a comprehensive and holistic way.

With respect to I, II and III, the framework keeps hazards and threats separate. The hazards (i.e., the stochastic failures affecting the CPS safety) are modelled by the Multi-State Physical Modeling (MSPM) approach for integrating the physical knowledge on the aging and degradation processes of the components.

A three-loop Monte Carlo (MC) simulation scheme is proposed for operationalizing the MSPM approach and for quantifying and controlling the confidence in the CPS reliability assessment, leveraging modeling detail with computational demand.

For threats (i.e., the malicious attacks affecting the CPS security) analysis, a MC-based simulation framework has been developed for generating cyber attack scenarios in CPSs and evaluating the effects of the cyber threats on the system functionality and integrity. This allows prioritizing the most vulnerable components and taking decisions on cyber security protection. A safety margin estimation approach is proposed for cyber threat prioritization. Safety margins are estimated by a Bracketing Order Statistics (OS) approach, with respect to one- and two-sided thresholds.

With respect to part IV of the work, on one side, to protect the CPS from (unknown and uncertain) cyber attacks, an Adversarial Risk Analysis (ARA) approach has been proposed for analyzing decisions between intelligent adversaries providing a novel one-sided (i.e., defender) prescriptive support strategy for optimizing the defensive resource allocations based on a subjective expected utility model. A MC approach has been embedded into the ARA model for treating uncertainties in the decisions of the adversaries, for improving confidence in obtaining the optimal defense resource allocation, leveraging robustness of protection actions on the CPS with uncertain malicious threats.

On the other side, the part IV of protection design has also presented the prompt recognition and distinction of cyber attacks from component failures in CPSs relying on the simultaneous treatment, within a consolidated Non-Parametric Cumulative Sum (NP-CUSUM) approach, of the measurements taken from redundant channels. The diagnostics approach has been demonstrated to be with very low false and missed alarm rates, with reference to a prespecified threshold, and very low misclassification rates varying with the reference delay differences.

In conclusion, the overall framework proposed in the PhD thesis provides results that help the analysts to identify hazards and threats of CPSs, analyze their causes, model their potential scenarios and consequences, and propose decisions for system protection and resilience, as shown in the application of the framework to a typical Reactor Protection System (RPS) of a Nuclear Power Plant (NPP) and to the digital Instrumentation and Control (I&C) system of an Advanced Lead-cooled Fast Reactor European Demonstrator (ALFRED)).