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DOCTORAL PROGRAM IN ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

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ADVANCED STEAM ACCUMULATION THROUGH VAPOR-LIQUID THERMAL ENERGY STORAGE TECHNOLOGIES

Abdullah Bamoshboosh - Supervisor: Prof. Gianluca Valenti

The objective of this work is to assess the possibility of exploiting vapor-liquid systems for thermal energy storage, in particular for steam. The opportunity of using vapor-liquid system arises from the fact that commercial phase change systems mainly exploit solid-liquid or solid-solid phase transition. These systems show generally good thermal energy storage capacities, both on a mass and a volume basis, but show poor heat transfer characteristics that cannot be overcome with simple systems. On the other hand, vapor-liquid systems show even larger heat storage capacities and much better heat transfer characteristics. They also show much larger volume variations, which has been the main reason those systems have not been studied in detail.

The steps performed in this work are:

- a tool to perform a fluid-independent generalized analysis of pure fluids and mixtures is built in order to better understand the behavior of vapor-liquid systems in closed and constant volumes;
- case studies are defined in order to apply the proposed technology;
- a tool to calculate the performances of the proposed system is developed and tested.

The fluid-independent analysis is deemed fundamental for two main reasons. The first reason is that multiphase closed and constant-volume systems do not have wide applications, and their behavior is generally not greatly understood. The second reason is that because of the novelty of this type of application, a tool that can be applied to diverse cases is needed. In order to be able to study the applicability of thermal energy storage with these systems, a tool capable of allowing the designer to find the characteristics of the optimal fluid for storage is required. This tool is based on the Lee and Kesler formulation of the Corresponding State Principle. A multicomponent and multiphase residual property calculator is built that works with temperature and specific volume definitions. The use of temperature and specific volume as input variables raises the need of introducing specific mixing rules for the critical properties, since the literature mixing rules are all designed for temperature-pressure definitions.

Subsequently, the tool is used to assess the heat storage capacities of different classes of fluids in different conditions. Firstly, the countercondensation mechanism is explained. This is the phenomenon for which constant volume systems at specific volume lower than the critical volume show an increase in the vapor fraction at temperatures close to saturation, which eventually goes to 0 and in the subcooled region, as can be seen in Figure 1. The first result is that complex molecules show the best heat storage characteristics. This is because of a combination of larger ideal gas specific heat and a steeper saturation curve. Subsequently, the main conclusion of this part of the work is that vapor-liquid systems can exploit a larger temperature difference if a trade-off with the mass of the system itself is accepted, resulting in potentially larger energy stored.
The analysis of mixture is then taken into consideration because of the possibility of tailoring the fluid characteristics to the required application. When analyzing mixtures, the potential increase in energy storage capacity is investigated by studying the effect of binary interactions parameters on multicomponent systems. It is shown that reasonable binary interaction parameters show little to no effect on heat storage, and that because of the inherent non-specific nature of the generalized analysis fluid mixtures result in weighted averages of the pure fluids themselves.

Subsequently, the detailed model of the heat transfer system is presented. Figure 2 shows the proposed layout of the thermal energy storage system. The model is built and designed in order to simulate the multiphase heat transfer from steam to the vapor-liquid storage system. Subsequently, two main case studies are defined: the first regarding solar thermal systems, and the second regarding medium sized, direct steam generation Concentrated Solar Power plants. The latter case is then analyzed in detail from a heat transfer point of view.
For Concentrated Solar Power plants, cyclic siloxane D6 is found to be the best option for thermal energy storage because of its high critical temperature and low critical pressure.. The application of D6 shows that the use of D6 would allow to increase the maximum storage temperature of about 55 K with respect to the current technology, which is steam accumulators, with a 25% decrease in the volume-based thermal energy storage capacity. This is not an issue, as the storage section of Concentrated Solar Power plants represent a small fraction of the total space occupied by the plant. Subsequently, the heat transfer performances of the proposed system are analyzed and compared with the current state of the art alternative for those systems, which is concrete-based energy storage. The storage is performed by using both D6 and steam, in order to highlight the differences related to the properties of the fluid. Firstly, it is shown that the heat transfer resistance of the vapor-liquid storage system is largely negligible. Secondly, it is shown that, because of its much larger heat transfer system, vapor-liquid systems are much more effective for storage. This is because the larger the energy stored in the same time, the lower the vapor fraction at the outlet, and thus the longer it will take the tank to reach the maximum pressure and stop storing excess steam from the solar tower.

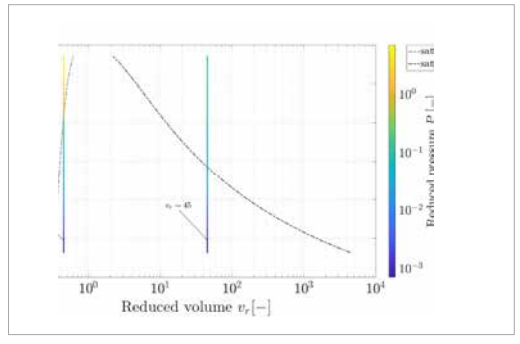

Fig. 1 - Reduced temperature, as a function of reduced volume, at reduced volume of 0.45 and 45, taken as example, for a hypothetical intermediate complexity fluid with acentric factor equal to 0.2, with colorbar for reduced pressure.

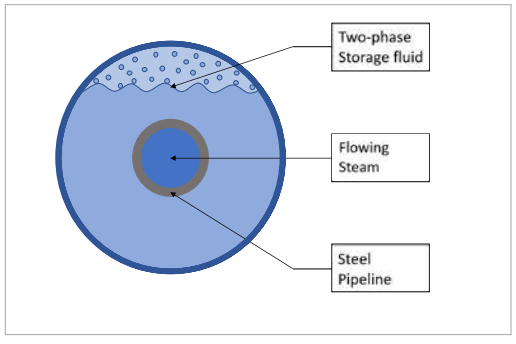

Fig. 2 - Representation of the section of the storage system.

TECHNO-ECONOMIC STUDY OF CHIMNEYLESS ELECTRIC ARC FURNACE PLANTS FOR THE COPRODUCTION OF STEEL AND OF ELECTRICITY, HYDROGEN, OR METHANOL

Camilla Nicol Bonacina - Supervisor: Prof. Gianluca Valenti

The steel industry is highly energy-intensive and is linked to the 7% of the global carbon dioxide emissions from the energy system. One of the key measures to decarbonize this sector is an increase in the share of recycling metal scrap in electric arc furnaces. This project aims at making more sustainable, more efficient and more economical the production of steel through the implementation of a chimneyless electric arc furnace route, whose products are fundamental for our lives. The scope of this work is to perform a techno-economic study of different plant configurations realizing the novel concept of chimneyless electric arc furnace plants fed either by scrap or direct reduced iron (DRI) for not only producing steel but also, alternatively, electricity, hydrogen, or methanol. First, different plant configurations are conceived based on the review of state of the art electric arc furnaces and reasoning on the best strategies to make the furnace plant chimneyless. The configurations are distinguished mainly based on: i) the feed material, i.e. scrap or DRI, ii) the electrolysis technology, i.e. solid oxide or alkaline electrolysis, iii) the management of the CO-rich gas from the furnace exhaust gas, and iv) the main product of the plant, i.e. electric power, hydrogen, or methanol. Secondly, a method to retrieve exhaust gas flow rate and thermodynamic conditions is developed to account for the changes in the process affecting the exhaust gas evacuation system. Thirdly, a numerical model is implemented in Aspen Plus to simulate the behavior of the system in the different proposed case studies, and Aspen Custom Modeler is used to calibrate the detailed model of the most significant unit in terms of costs, i.e. the electrolyzer. Then, green power plants, i.e. wind, solar and nuclear, are designed for electricity production and validated via both literature and experimental data. Finally, an economic analysis is performed to analyze the competitiveness of the different configurations and, then, compare them.

Overall, the feasibility study of the plant leads to promising results in all the case studies analyzed. Among the mass balance results, i) the steam produced in the heat recovery unit allows to completely recover all the carbon present in the furnace exhaust gas, ii) the oxygen produced by electrolysis can be used for performing postcombustion of carbon monoxide (when present), and iii) direct emissions of carbon dioxide are almost nulled. In terms of energy balances, the net electric power input ranges from 235 to 991 kWh/tsteel with DRI-fed furnace configurations less energy intensive. Renewable energies allow reductions of indirect carbon dioxide emissions up to 60 tCO2/h.

In terms of economic viability, the configurations are characterized by highly variable internal rate of returns. DRI-fed configurations are more viable than scrap-fed ones due to both the more efficient methanol synthesis and absence of carbon capture costs. Electrolysis (when present) represents the highest fraction of the costs. The effect of the electricity price on the viability of the case study is significant. Indeed, in the optimistic scenario (low electricity and electrolyzer investment cost) the internal rate of return varies between 20 to 45% for scrap-fed cases and between 49 to 73% in DRI-fed cases when hydrogen or methanol are produced. In the pessimistic scenario (high electricity and electrolyzer investment cost), only DRI-fed cases with methanol and hydrogen production are viable with internal rate of returns of 10% and 2%, respectively. The competitiveness of case studies with power production only is not affected considerably by the scenario assumptions, with the scrap- and DRI-fed cases characterized by internal rate of returns of around 9-10% and 73-78%, respectively.

In the optimistic scenario, alkaline electrolysis results are comparable with the solid oxide technology ones with the latter more viable due to the lower electric energy consumptions. However, if the electricity cost increases to 100 €/MWh, the only viable case with alkaline electrolysis is the DRI-fed furnace one with methanol production with an internal rate of return of 14%.

The hydrogen and methanol costs that null the net present value are compared to expected future hydrogen prices of 2 €/kg and current methanol prices of 350 €/t when electricity is purchased from the grid for sake of example. In the scrap-fed cases, hydrogen and methanol are competitive only for low electricity costs. In the DRI-fed cases, methanol is competitive for any electrolyzer and electricity costs. Hydrogen turns out to be competitive only when the electricity cost is low. The scrap-fed configuration with sole electricity production turns out to be more competitive than the one with methanol production when the electricity cost is high. Being the scrap- and DRI-fed furnaces located in different countries, the solar and wind plant will be affected by the weather conditions and by the costs of electricity production. Analyzing all the case studies and power sources, the levelized cost of methanol ranges from negative values to a maximum of 742 €/t. The levelized cost of hydrogen ranges from negative values to a maximum of 4.7 €/kg. For the pessimistic scenario, in the scrap-fed cases the less and more competitive power sources are the grid and nuclear ones respectively, while in the DRI-fed cases the solar and nuclear respectively. For the optimistic scenario, in the scrap-fed cases the less and more competitive power sources are the wind and grid ones respectively, while in the DRI-fed cases the grid and solar respectively.

Then, the net present value analysis shows that economic results can be improved if a steel premium is introduced in the economic calculations. Considering a methanol and hydrogen selling price of 400 €/t and 3 €/kg, steel premiums higher than 25 €/t and 0 €/t attain positive net present values for a relatively high electricity cost of 100 €/MWh in the scrap- and DRI-fed configurations, respectively. This means that applying a relatively low steel premium, e.g. 6%, it is possible to increase further the competitiveness of the novel proposed plant configurations.

In conclusion, the novel chimneyless electric arc furnaces result to be feasible on a technical and economic point of view. Generally, the configurations of DRI-fed furnaces allow to obtain more viable results with respect to scrap-fed furnaces, and the competitiveness of sole electricity, hydrogen or methanol production configurations depends on the case study analyzed, the power source and, especially, on future trends of market prices.

DEVELOPMENT OF ADVANCED NANOCERAMIC COATINGS FOR NUCLEAR FUEL CLADDING IN PRESSURIZED WATER REACTORS

Mattia Cabrioli – Supervisor: Dr. Fabio Di Fonzo
Co-Supervisor: Prof. Marco Beghi

The inherent potential risks associated to the zircaloy cladding/UO_2 fuel system hinder the improvement of safety and reliability of commercial nuclear reactor technology. The need for more efficient and reliable plants in the global energy production scenario became manifest after the Fukushima Daiichi event. In this framework, the worldwide research effort was prompted to develop new active and passive safety systems, specifically regarding nuclear fuel and readily implementable in active plants. Accident Tolerant Fuel technology is based on these concepts and, in its short-term evolutionary design, is targeted to enhancing the strengths of commercial zircaloys and improve their resistance to severe degradation during design-basis (DB) and beyond design-basis (BDB) accidents.
The research plan and experimental activities conducted by the candidate were completed in the framework of the Horizon 2020 project IL TROVATORE, aimed at identifying, optimising, and validating the most promising ATF cladding concepts for Generation II/III Light Water Reactors (LWR), with focus on Pressurised Water Reactors (PWR).
Looking at the coolant/cladding side of the reactor fuel, a suitable surface modification of standard cladding was chosen, more specifically by coating its external side, to minimise the impact of any modification introduced to the current fuel design. Hence the main target was to prevent accelerated corrosion and failure of fuel cladding of PWRs during normal operation and one case of DB accidents represented by Loss of Coolant Accident (LOCA), which played an important role in the chain of events that led to the Fukushima disaster.
Ceramics, in particular metal oxide compounds, were chosen as best candidates for coating material because of their inertness to water corrosion and high temperatures. Since the possible reactions between various compounds and water at different temperatures are peculiar of each oxide, a screening phase constituted the first step of the selection process. Pulsed Laser Deposition (PLD) was then employed to apply coatings of candidate materials on zirconium and zircaloy substrates. Fine tuning of PLD process parameters allowed the deposition of dense coatings which would act as efficient barriers against penetration of corrosive media, whilst preserving the microstructure of the substrate.
PLD-Cr_2O_3 coatings were proposed as single layer solution. Chemical compatibility with simulated PWR water and steam at high temperature were assessed. Moreover, the thermodynamic stability of the Zr/Cr_2O_3 system at relevant temperatures was investigated. PLD process was optimised to obtain dense coatings with thickness in the range 1-10µm and a resulting non-crystalline structure, as determined by X-ray diffractometry (XRD). Static autoclave tests in simulated PWR core temperature, pressure and chemistry up to 30 days, demonstrated the compatibility of PLD-Cr_2O_3 with PWR coolant under normal operating conditions, with reduction of 40% in the surface-normalised weight gain of specimens coated with 1µm Cr_2O_3 films with respect to uncoated reference.
Atom Probe Tomography was carried out to investigate the critical interface coating/substrate, to evaluate any possible chemical interaction and oxidation of the Zr substrate at the nanometric scale. Anticipated interactions at the Cr_2O_3/Zr interface at high temperatures (T>800°C) were evaluated by means of annealing experiments in vacuum, inert gas, and steam/inert gas atmosphere. Post-treatment analysis confirmed Cr_2O_3 reduction and Zr oxidation at coating/substrate interface, representing a potential shortcoming during LOCA events because of the associated risk of degradation of cladding properties up to ultimate failure, independently on the thickness of Cr_2O_3 coatings. This analysis suggested that under LOCA conditions a single layer of Cr_2O_3 could be insufficient to mitigate the two main drawbacks of commercial zircaloys at high temperatures, namely the reduction of pristine metallic cladding thickness by oxidation, and H_2 generation. Consequently, the efforts were dedicated to mitigating the coating/interface reactions at high temperatures by means of an interdiffusion barrier layer.
Y_2O_3 was identified as the best interlayer material because of its higher thermodynamic stability with respect to Zr, Cr and Cr_2O_3 in the whole range of temperatures and pressures typical of normal operations and DB accidents in PWRs. PLD-grown Y_2O_3 coatings were applied as interlayer for blocking interdiffusion between Zr and other materials, in particular Cr. The lack of reliable data on Zr-Y_2O_3 interactions available in thermodynamic databases prevented the calculation of driving forces for interactions at the Zr/Y_2O_3 interface. Therefore, the candidate's research activity provided new experimental data about such system.
The effectiveness of Y_2O_3 was addressed for the specific case of prevention of Zr-Cr interdiffusion, as the most relevant for industrial application, in the prototypical system Cr/Y_2O_3/Zr. First PLD-Y_2O_3 coatings were applied to Zr-based substrates, then Cr coatings with compact columnar structure were applied by magnetron sputtering (MS) deposition. The MS technique was employed to replicate on a laboratory scale what is envisaged by fuel providers for commercial production.
Compatibility tests were carried out on double-layer coated Cr/1µm Y_2O_3/Zircaloy-4 tube segments by means of exposure to high temperature in flowing Ar/steam mixture at temperatures in the range 1200°C-1600°C. Measurements of H_2 gas produced by the samples were employed as real-time quantification to assess the resistance of the coated cladding to oxidation during the above-mentioned kind of accidents. The point of transition between protective and unprotective behaviour of the coating for the Cr/Y_2O_3/Zr system, was found at a temperature of 1420°C, which is about 70°C higher than the value for the Cr/Zr system proposed by nuclear fuel companies and tested under the same experimental conditions. This significant achievement translates in an improved tolerance of fuel cladding to LOCA and potential BDB subsequent transients. Since clusters of Zr and ZrO_2 were detected at the oxidised-Cr/Y_2O_3 interface at temperatures higher than 1200°C, a set of experiments was specifically designed to identify the possible mechanism which could induce a diffusion of Zr through the Y_2O_3 interdiffusion barrier layer in the range 1200-1450°C for 1h.
On a parallel track, preliminary static autoclave tests for compatibility assessment of the double-layer coated Cr/Y_2O_3/zircaloy-4 tube segments with PWR coolant were conducted. Since the outcomes put in evidence a potential issue for the Cr/Y_2O_3/Zr system in contact with water during normal reactor operation, a new set of tests was designed. Previous research demonstrated the excellent performance of Cr coatings on Zr, hence the critical component could be represented by the interdiffusion barrier itself. Y_2O_3/Zr specimens without external layer of Cr were exposed in static autoclave, to maximise the interaction rate of Y_2O_3 with water and simultaneously recreate the possible scenario of damaged outer Cr coating which exposes the interlayer. Visual examination and SEM analysis confirmed the deterioration of Y_2O_3 upon exposure to simulated PWR coolant by adsorption of water and formation of hydroxides, resulting in severe coating delamination. In view of the industrial application of the coatings under investigation, phenomena of this kind would prevent the beneficial effect of interdiffusion barrier and consequently need to be avoided. For this reason, new formulations of PLD-Y_2O_3 coatings were identified and evaluated to prevent coating failure during normal operation of the reactor. The effect of materials and composition were evaluated and through the proper combination of composition and fabrication process, the stability of coating under exposure to PWR water was achieved.

OPTIMAL DESIGN AND OPERATION OF AGGREGATE ENERGY SYSTEMS UNDER UNCERTAINT

Alessandro Francesco Castelli – Supervisor: Prof. Emanuele Martelli

Tutor: Prof. Paolo Chiesa

This thesis focuses on the optimal design and operation of Aggregate Energy Systems (AES) under uncertainty. These systems are composed by different dispatchable storage and generation units, as well as non-dispatchable, distributed energy sources. They are designed with the purpose of integrating different energy technologies so to improve the overall efficiency, meet different energy demands and facilitate the penetration of renewable energy sources. Much interest is nowadays present for these systems, since they are already economically competitive in certain applications (e.g., serving heat, power and cooling for industrial and urban users) and expected to play a major role in the energy sector. In literature different kinds of Aggregate Energy Systems can be found: Multi Energy Systems, microgrids, Virtual Power Plants, etc. Virtual Power Plant differentiate themselves from the rest since they are designed with the main goal to participate in the electricity markets, and they usually feature a larger installed power.

Given the presence of different technologies and the complexity of the system, both the optimal design and operation require the development of mathematical tools able to capture the different technical aspects of each unit as well as the uncertain nature of the parameters (e.g., PV generation). In this Thesis, four topics of industrial interest are considered and analyzed, and four different approaches are proposed. These are: (1) a Rolling Horizon approach for the optimal robust operation of Aggregate Energy Systems featuring yearly constraints and/or seasonal storage; (2) a multi-stage stochastic optimization model for the optimal operation of Virtual Power Plants participating in the electricity markets; (3) a two-stage stochastic optimization model for the optimal design of Aggregate Energy Systems with *(N-1)*-reliability; (4) a methodology for the optimal design of zero carbon emission Virtual Power Plants with hydrogen seasonal storage. When applied to real-world case studies, the approaches resulted successful in the tasks they were designed for. At first, the optimal robust operation evaluated by the Rolling Horizon (1) was able to serve the user's energy demands through an entire year and for all the case studies considered. In addition, the considered yearly constraints were met and the daily management of the seasonal storage proved to be successful in avoiding shortages.

Regarding the study on the Virtual Power Plant (2), the multi-stage stochastic optimization model was effective in carefully modelling both the energy systems and the electricity markets, and the solutions obtained proved to be better than the ones obtained with a deterministic approach. Moreover, the computational time was significantly improved by developing a shrinking horizon-based decomposition, making the methodology suitable for practical industrial use.

For what concerns the third research topic addressed in this thesis (3), the two-stage stochastic model for the optimal design of Aggregate Energy Systems with *(N-1)*-reliability was able to compute design solutions able to meet the users' demands along a whole yearly horizon, for whichever contingency. The long solution time required the development of decomposition techniques, one of them very effective in reducing the computational time although not guaranteeing optimality.

Finally, the optimal design of a future Virtual Power Plant featuring hydrogen storage and hydrogen-fired combine cycles was evaluated (4). The proposed methodology combines some of the features presented in the previous works, such as many parts of two-stage stochastic model of (3), the reserve constraints present in (2) and a modified version of the Rolling Horizon for the optimal schedule of the plant and seasonal storage management presented in (1). Results proved these concepts and evaluated the techno-economic feasibility of such aggregate system.

In conclusion, the methodologies presented in this Thesis were proven to be effective for the considered real-world case studies, although improvements can be made in terms of computational time and ease of implementation.

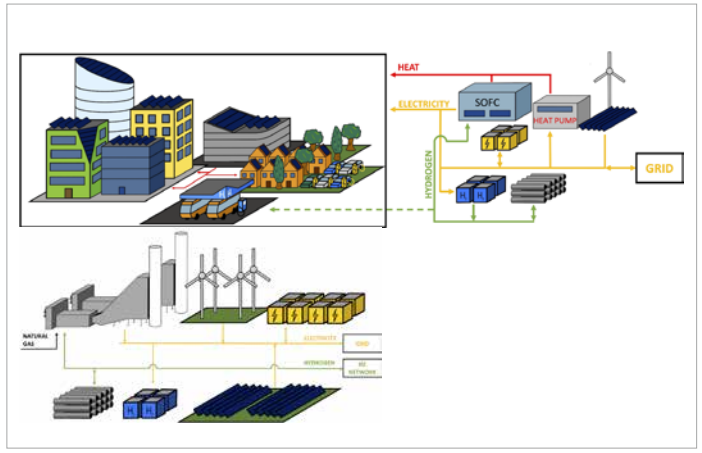

Fig. 1 - Two examples of AES: a Multi-Energy System serving urban users (top), and a Virtual Power Plant operating in the electricity markets.

A NEW THERMOGRAPHIC TECHNIQUE APPLIED TO ADVANCED TWO-PHASE HEAT TRANSFER DEVICES

Riccardo Clavenna - Supervisor: Prof. Lucio Araneo

Throughout this thesis, the novel Twin Background Subtraction (TBS) technique evolved from a theoretical concept into a validated, innovative, non-intrusive wide field of view measurement method. This method enables investigations into the behaviour of thin liquid films. Unlike techniques that are available in the literature, the developed method can simultaneously measure the thickness and the cross-sectional mean temperature of the liquid film.

This innovative method uses infrared images from a middle-wave infrared camera, providing a broader field of view compared to many local techniques. Three different test campaigns were conducted:

- Fine-tuning of the TBS technique with a thin layer of confined water.
- Laboratory testing of the technique applied to a section of a pulsating heat pipe (PHP).
- Parabolic flight tests under microgravity and hypergravity of the same PHP.

The initial primary focus of the research was the experimental aspect, as numerous challenges were met in obtaining precise and accurate measurements. The design of the experimental setup was a crucial aspect in determining the technique's reliability and accuracy. During the preliminary phase, a theoretical and experimental campaign was conducted to determine the goodness of the technique.

The TBS technique's applicability across an extensive range of film thicknesses was demonstrated. For water films, the uncertainty in thickness measurements was less than 5% for thicknesses between 50 and 350 µm, suggesting wider applicability than the one in the theoretical uncertainty estimation, where the applicability range was calculated to be 15µm-160µm. Qualitative results were also valid for microfilms as thin as 10 µm in which the relative error was high, but the film qualitative trend was valid. However, thinner films led to substantial errors and unrealistic measurements as the attenuation of the microfilms. Temperature measurement accuracy reduced with increasing film thickness, and like thickness measurements, the uncertainty became infinite as the film thickness approached zero. The error also depended on the film temperature and the temperature difference between the two backgrounds. The film temperature is optimal when it lies in between the temperatures of the two emitting backgrounds behind the film. A larger temperature difference between them results in increased attenuated signals difference enhancing the technique's accuracy.

The TBS technique was applied to a PHP with a 3 mm ID during the experimental campaigns, focusing on dynamic measurements of film thickness and temperature.

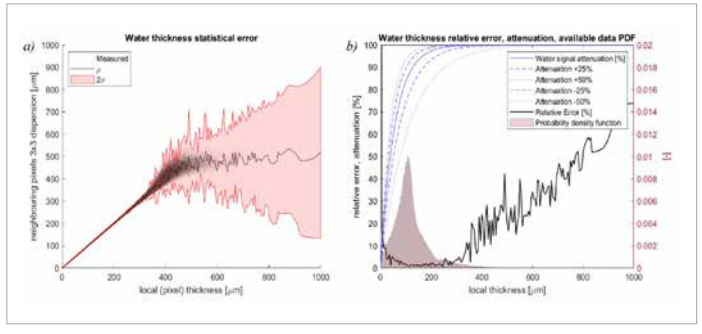

Fig. 1 - a) Thickness absolute error; b) thickness relative error, and signal attenuation.

This innovative application contributes significantly to the research on PHPs, allowing for an in-depth study of thin liquid film behaviour within these systems. It potentially enables the narrowing of the gap between simulations and experimental results, improving model accuracy and offering new insights into the dynamics of PHP.

During this stage, the technique's accuracy has been improved through multipoint calibration, accounting for film temperature and thickness effects. The application of the TBS to the PHP included the simultaneous acquisition of direct and mirror-reflected IR images as well as a greyscale high-speed recording. The experimental campaigns studied the PHP at different power levels in a gravity-changing environment. From the results of these two latter campaigns, the working limits were 20-350µm thickness with ethanol as the working fluid. Statistical analysis in the range between 0-350µm revealed that temperature and thickness were linearly dependent on thermal power above 105W, with a more stable thermal response. Lower power levels caused the device to deactivate under normal or hypergravity. The results emphasize the technique's potential for studying a variety of thermofluidic problems while considering film temperature and thickness effects.

The TBS technique has the potential to offer significant advancements in the field of thermofluidic research, providing a practical experimental approach for studying complex phenomena such as condensation, confined flows in channels, and flow boiling. The technique is a promising tool for research and development in this field.

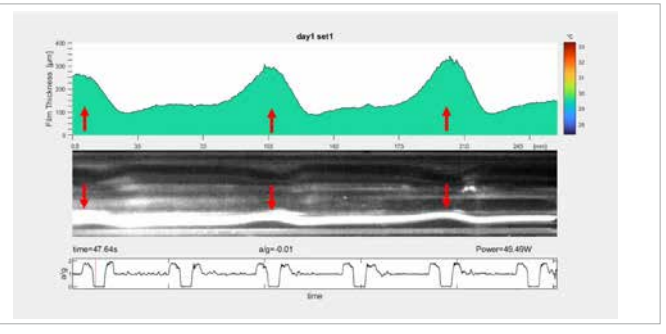

Fig. 2 - Frame of the PHP during microgravity.

UNDERSTANDING AND MITIGATING DEGRADATION OF PEMFC CAUSED BY REAL AUTOMOTIVE OPERATION

Elena Colombo - Supervisor: Prof. Andrea Baricci
Tutor: Prof. Andrea Casalegno

Summary The research on automotive Proton Exchange Membrane Fuel Cells (PEMFCs) must improve the technology durability to increase the commercial diffusion. This work aims to clarify the degradation mechanisms of real operations at a local level, analysed in dependence on specific operations. I evidenced the growth of catalyst nanoparticles as the main aging process: lot of effort was spent to explain its drivers, focusing on voltage cycles. I proved the critical role of transitions to low potential, relevant during the short stops. As useful tools for a systematic study, new representative Accelerated Stress Tests (ASTs) were designed on an innovative zero-gradient hardware. The outcome consists in accelerated methods for lifetime evaluation that combine both an experimental and a modelling approach. The comprehension of still little-known aspects of PEMFC aging was broaden, serving as a basis to develop mitigation strategies.

Introduction There is a urgent need for sustainable technological solutions to face the environmental challenges. Europe is planning to reach the full climate neutrality by 2050. A carbon neutral transport sector needs appropriate solutions that start from an energy provision based on renewable sources. The renewable energy can be used to produce hydrogen via electrolysis, then exploited in fuel cell electric vehicles (FCEVs). FCEVs penetration is expected in both passenger and heavy-duty vehicles and PEMFCs are considered as the most mature technology for this purpose. Nonetheless, even after decades of research, fundamental and applicative studies are still necessary to overcome some technical barriers, which are cost and durability. The cost is driven by the presence of expensive components, like Pt/Pt-alloys nanoparticles used as catalyst and perfluorinated acid membranes. Objectives are to reduce or to replace these components by cheaper. However, solutions researched for cost reduction are detrimental for components lifetime and degradation can be enhanced by specific or inappropriate operating conditions. Lot of studies have been already reported in the literature to elucidate the fundamentals of aging. However, there is still the necessity to provide information that reflect what occurs *operando* in the real-world.

Methodology This PhD work provides a contribution to the critical topic of PEMFC degradation. I followed a doubled approach, based on a wide experimental campaign on state-of-the-art Membrane Electrode Assemblies (MEAs) and a physical interpretation of the aging phenomena through a modelling activity. I moved towards a progressive simplification of a complex problem, while getting deeper into the physical comprehension. First, I studied a dynamic load cycle representative of real-world, that I then separated into its units of operation and detailed through *ad hoc* accelerated protocols which clarified the stressors that rule the decay.

Realistic aging comprehension Since the lack of protocols which truly reflects vehicles on the road, the European ID-FAST project consortium developed a representative and complex stack dynamic load cycle, which I adapted to test single cells in a segmented hardware: this setup ensures a local level analysis, from the cell air inlet region to the outlet. The cathode catalyst layer was the mainly aged component, combined to alterations of the membrane. Degradation phenomena cover mechanisms which are both reversible (*i.e.* loss can be recovered) and irreversible: I analysed these contributions in dependence on specific events (stop procedures) and operating modes (low and high power). I detected the loss of the catalyst active surface area as the dominant irreversible mechanism, due to the electrochemically unstable behaviour of the Pt nanoparticles (*Ostwald ripening*). The Pt active area showed a rapid decay in the first 200-400 operating hours and the transmission electron microscopy images confirmed a prominent nanoparticles increase in size from 4.4 nm to 6.5 nm, at which value they stabilized. The process is almost uniform in all the cell regions. However, in terms of performance, the air-inlet was the most aged area, with a prominent loss at the highest loads apparently connected to an alteration of the ionomer thin-film inside the catalyst layer, proved due to the low humidification.

Development of accelerated tools for lifetime prediction Since complete and realistic degradation tests are extremely costly and time consuming, ASTs are usually exploited for a rapid evaluation of PEMFC materials. However, those commonly adopted lack of representativeness because they exacerbate the operating conditions outside the boundaries of the application and exploit an inert atmosphere. With the aim of being fast but not to lose the connection to the real-world, we proposed a new operational "Combined hydrogen/air AST", thought for a zero-gradient hardware. This hardware keeps the MEA under uniform conditions: it is specifically intended to quantify the materials performance without accounting for any interdependency between the MEA layers and the setup design. We also proposed an innovative and open configuration, which allows to further save time through the simultaneous testing of four MEAs. The results of the Combined AST, which mimics both low and high power operations, were correlated to the results of the dynamic load cycle: I identified a 10-fold acceleration, while keeping the coherence of degradation mechanisms, proving the effectiveness of the methodology.

Stressors for catalyst instability The peculiarities of the Pt active surface area decay observed under real world aging required to detail the catalyst degradation topic. I designed a wide experimental campaign focused on the voltage profile under hydrogen/air, devoted to study potential window and transitions. ASTs conditions were restricted to those encountered in real vehicles (≤0.90 V) and short stops parameters where largely detailed. Short stops are a technical procedure consisting in feeding hydrogen while interrupting the air supply to avoid air leakages at the anode compartment: the cell voltage decreases to almost 0 V. An unexpected acceleration was observed in presence of very low voltage transients (<0.4 V), overlooked by the literature so far. I developed a numerical model to provide a physic-based description for a still unexplained share of degradation: a new cathodic dissolution formulation is proposed, concomitant to the removal of some stable oxides, which were quantified by tuning a new *in situ* method.

Impact of the research The findings of this work will accelerate the development of PEMFC system mitigation strategies, as well as of innovative materials able to increase the durability of state-of-the-art catalyst layers of PEMFC. The outputs are useful to orientate the selection of the operational constraints for reaching the durability targets of the automotive (8'000 hours) and the heavy-duty sector (25'000 hours). In order to limit the non-homogenous degradation, mitigation strategies must pay attention to the low load functioning and to the operating conditions of the air inlet area, mostly in terms of humidification state. This work established the impact of urban switch-offs in driving the irreversible Pt active surface area decay: limiting the upper potential, as usually done, seems not a sufficient expedient. Mild effects of mitigation were identified working on the humidification state of the stops and on the potential sweep velocity. A trade-off must be identified between the performance enhancement due to Pt oxide removal and the necessity to limit the catalyst nanoparticles growth because of the suspected contemporary Pt dissolution.

TRANSIENT SIMULATION AND EXPERIMENTAL STUDY OF THE GAS-FIRED AMMONIA-WATER ABSORPTION HEAT PUMP SYSTEMS: DEVELOPMENT OF AN EFFICIENT NUMERICAL FRAMEWORK

Babak Dehghan - Supervisors: Prof. Mario Motta, Prof. Livio Mazzarella

In recent years, the interests in absorption heat pumps (AHPs) have escalated due to the worldwide efforts in decreasing the use of fossil-based vapor compression system. Absorption heat pumps used in residential and commercial applications encounter transient variations in operating conditions such as ambient temperatures, driving heat source temperatures and heating or cooling loads. Absorption heat pumps operating in buildings experience multiple start-up and shut-down cycles daily or hourly. Hence, if system performance is not controlled during these transients, low operating efficiencies will result in a significant portion of the run-time, leading to significant power losses. To minimize these losses and associated operating costs, it is critical to optimize the dynamic performance of the chiller. Such optimization becomes very challenging because of the two loops in the absorption heat pump (the refrigerant loop and absorbent loop) that both require multiple control variables such as the condenser and absorber fan speeds, two valve settings and pumping rate.
A robust control algorithm is needed during such start-up and shut-down operations and would determine the optimal flow rates and valve settings for the given operating condition that maximizes the chiller performance. In general, controlling a vapor-absorption system is more difficult than controlling a vapor-compression system because two fluid loops in liquid and vapor phases at different species concentrations must be tracked, thus involving more parameters to be controlled. The development of such a control algorithm requires a thorough understanding of the transient behavior of the absorption system.
Figure 1 compares the potential COP variation of an absorption system with and without controls. As mentioned previously, the most suitable control logic can be defined using the reliable dynamic model and consequently leads to performance improvements of the AHP.

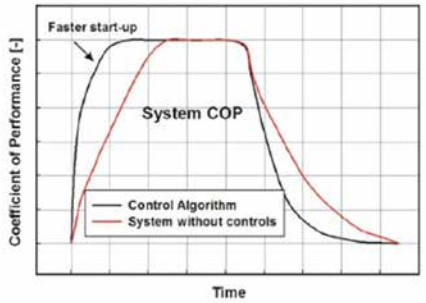

Fig. 1 - Potential performance improvement of the AHP by a suitable control algorithm (Viswanathan et al.)

In this PhD research two important aspects of AHPs (steady state and dynamic behavior) are analyzed and finally an efficient experimentally validated numerical framework which is able to predict transient behavior of the AHPs with high accuracy has been developed.
As mentioned, the research is divided into two parts as follow;
Part (a): Steady state and seasonal performance analysis of three AHP cycles; When designing a gas driven heat pump, the selection of the cycle impacts both on complexity and efficiency. Among absorption cycles, the nominal efficiency usually increases with complexity. However, heat pumps are required to operate over a wide range of conditions, of different temperatures and capacity. In the first part of current thesis, three alternative cycles, i.e single-effect (SE), generator-absorber heat-exchange (GAX) and vapor-exchange (VX) for a gas-driven air-source ammonia-water absorption heat pump are compared, considering small-scale space heating as target application. For each cycle, both full-load under various temperature conditions and seasonal performances are predicted by means of numerical simulations. Small capacity appliances are usually equipped with fixed geometry restrictors, meaning that the solution mass flow rate is driven by the pressure difference across the associated restrictor valve. This feature is included in the modeling assumption as it affects the temperature of the generator and, ultimately, the performance at the various conditions. At full load, the VX cycle resulted in achieving the highest Gas Utilization Efficiency (GUE), followed by the GAX and SE. The differences among the cycles are higher at low thermal lift conditions, where the GAX effect is achieved in both the GAX and VX cycles, while are limited at high thermal lift. Looking at the seasonal performances, calculated on the basis of the method prescribed in the European standard EN 12309, the differences among the cycles became much narrower, with the Seasonal GUE ranging between 1.427 (SE) and 1.493 (VX). The small differences in terms of seasonal performances are explained considering that, in the prescribed working conditions, the GAX effect is only partially exploited.
Part (b): Transient Behavior assessments of a Single-Effect Ammonia-Water Absorption Heat Pump System; In the second part of the PhD research which is also the main part and objective of the PhD thesis, the long-term transient response of a single-effect ammonia-water gas-fired absorption heat pump prototype is investigated both numerically and experimentally. For the numerical model, heat and mass transfer components are divided into four groups: (a) tubular heat exchangers comprising condenser, evaporator, absorber, solution and refrigerant heat exchangers, (b) tray column heat exchanger comprising gas-fired generator, (c) refrigerant and solution tanks, (d) solution pump and restrictors. Components of groups a-c are modelled based on discretized volumes in which the unsteady mass, species and energy conservation equations are imposed, whereas solution pump and restrictors are idealized as algebraic models. The experimental analysis covers a period of over 10 hours, during which various step changes are applied to system inputs like gas power, inlet water temperature, solution and refrigerant flow rates, and brine inlet temperature. The results of the numerical model are compared with the experimental data which show good agreement in both transient and near steady state operation. Results show that, during transient operation average deviations are less than 2.94% and near steady-state conditions are less than 1.70%. The accuracy of the numerical model in predicting both the transient response and the steady-state values of the measurable outputs, makes it a valuable tool to gain insight on the internal dynamics of ammonia-water absorption heat pumps and cut down costs on time-consuming optimization experiments, such as the fine-tuning of initial solution charge, the implementation of a suitable concentration control strategy and the performance optimization at full and partial loads.

MULTIPHYSICS MODELLING OF SOLID FISSION PRODUCTS TRANSPORT IN THE MOLTEN SALT FAST REACTOR

Andrea Di Ronco - Supervisors: Prof. Antonio Cammi, Prof. Francesca Giacobbo, Prof. Stefano Lorenzi

Tutor: Prof. Francesca Giacobbo

Research on liquid-fuel reactor concepts has gained renewed interest over the last decade. Among them, the Molten Salt Reactor (MSR) and, in particular, the fast spectrum MSFR (Molten Salt Fast Reactor) has obtained a leading role as one of the selected Generation IV reference technologies. The adoption of a circulating liquid fuel, in conjunction with the fast neutron spectrum, makes the MSFR system unique from the design and modelling viewpoints. Internal heat generation, fuel thermal feedback and transport of delayed neutron precursors and fission products lead altogether to a strong intrinsic coupling between thermal-hydraulics, neutronics and fuel chemistry (Fig. 1). Reactor modelling efforts have therefore shifted towards full-core and multiphysics analysis to meet the requirements and complexity of physical and computational models for the MSFR.

Fission products (FPs) represent a major challenge in the modelling and design of the MSFR. They originate within the fuel and are not retained by solid structures, being thus free to be carried by the liquid fuel along the primary circuit. Some FP species are not expected to form stable compounds with the constituents of the fuel salt mixture and therefore may give rise to separate phases, either in the form of solid precipitates or gas bubbles. Solid FPs are likely to deposit on reactor surfaces in the form of solid precipitates, giving rise to potential issues such as formation of localised decay heat sources as well as deterioration of heat exchanger performance. Surface deposits might also pose a serious radiological threat in inspection/maintenance operations. Nevertheless, the study of FPs transport has found limited space in recent MSFR literature, and the analysis of the MSFR by means of a traditional system code approach is made difficult by its peculiar geometry and fuel circulation, making the use of high-fidelity models a more appropriate choice. The subject of this thesis is therefore the integration of transport models for solid FPs in state-of-the-art MSFR multiphysics tools, and to perform a preliminary analysis of FPs transport and deposition in relevant simplified MSFR cases. The development platform is the C++ open-source finite-volume CFD library OpenFOAM. Such approach is intended to allow for the analysis of inherently two- and three-dimensional effects, such as transport in complex turbulent flows, the estimation of particle deposition fluxes directly from concentration fields and the interaction with the gas bubbling system. Local temperature effects on precipitation of metallic species can also be directly taken into account, in view of coupling with thermochemistry calculations.

The contents of this thesis can be summarised as follows. A multiphysics approach based on an advection-diffusion-decay model is first described and then integrated in an incompressible single-phase multiphysics MSFR OpenFOAM solver. The implementation is verified, for simplified test cases, against analytical solutions derived from the well-known Graetz problem. Results show the good agreement, proving the correct implementation of the transport and deposition mechanisms considered and the capability of OpenFOAM in treating coupled deposition and decay phenomena of different relative intensities. Then, the developed models are tested on relevant two-dimensional MSFR cases, to conduct a preliminary analysis of FPs transport and deposition. Potential numerical issues arising from the commonly adopted "perfect adsorption" wall boundary conditions are addressed. Previous analytical results are also used to illustrate such issues, and are compared to numerical simulation in a lid-driven cavity. Due to their direct effect on transport, different turbulence modelling approaches are tested in a more realistic two dimensional MSFR case. It is observed that steep FPs concentration gradients are produced, and therefore significant mesh refinement in the wall regions is needed to correctly resolve the boundary layers. The comparison of three different common turbulence models, namely the standard k-ε, the standard k-ω and the k-ω-SST models, shows a significant influence on the particle concentration distributions, given the discrepancies in the predicted velocity and eddy diffusivity fields. However, the deposition rates, which are one of the main subjects of the study, are much less affected. This effect is probably due to the fact that, in the concentration boundary layer, transport is dominated by diffusion and turbulent diffusivity vanishes at walls. Furthermore, results from a preliminary simplified test case show a non-negligible role of precipitation modelling on the distribution of solid precipitate particles, suggesting the need for further developments. Finally, a preliminary LES multiphysics model of the MSFR is developed, relying on the multiphysics incompressible single-phase solver developed and described earlier. The use of LES as a dynamic analysis tool for the MSFR is essentially a new and fascinating research topic, with a wide range of potential applications. Here, a 3D MSFR geometry is developed and used to test different LES SGS models available as part of the OpenFOAM library. Transient simulation evolving in free dynamics from steady-state conditions shows, qualitatively, no significant discrepancies among different models in terms of frequency and amplitude of the turbulent oscillations introduced by LES modelling, suggesting their substantial equivalence for the dynamic analysis of the MSFR. On the other hand, predicted transients show non-negligible effects due to turbulence on main reactor integral parameters. These preliminary results might suggest the insurgence of interesting dynamic phenomena and new challenges for dynamics and control of the MSFR.

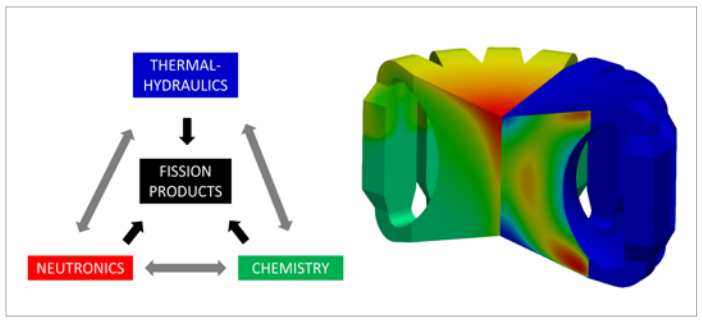

Fig. 1 - Multiphysics coupling between thermal-hydraulics, neutronics, fuel chemistry and fission products (left) and a 3D computational model of the MSFR (right).

A NEW DATA-DRIVEN LIFE CYCLE ASSESSMENT TOOL AT THE URBAN SCALE: THE CASE OF THE MILAN BUILDING STOCK ANALYSIS TO REDUCE THE RELATED ENVIRONMENTAL POTENTIAL IMPACTS

Jacopo Famiglietti - Supervisors: Prof. Mario Motta, Prof. Livio Mazzarella

Given the ambitious targets for greenhouse gas emissions reduction set by the European Union and the importance of cities in achieving these goals, there is an increasing need to analyze a city's environmental footprint with a life cycle approach. The life cycle assessment is considered the leading methodology for environmental metrics, permitting a holistic environmental perspective on cities. Developing a complete life cycle assessment can be difficult and time-consuming, particularly discouraging to non-experts. Life cycle assessment software applications are aimed at single product evaluation, making urban scale, data management and environmental assessment complicated or impractical, mainly due to the massive data processing required. The novelty of this work is a new tool, utilizing a data-driven approach, that allows an extensive environmental evaluation of buildings (following the EN 15978 standard). The tool was applied to analyze the city of Milan. Approximately 240 000 building units were investigated and compared using as activity data the information described in the Energy Performance Certificates (EPCs) of building units, collected in the OpenData CENED database (for the Lombardy Region), plus information from other libraries, i.e., the Geoportal of the Lombardy Region, TABULA, and the cadastre of thermal plants (CURIT). The tool uses ecoinvent 3.9.1 EN 15804 as a secondary database and the Environmental Footprint 3.1 EN 15804 and the Cumulative Energy Demand (primary energy – not renewable) – characterization methods. Figure 1 represents the building stock analyzed, corresponding to about 35% of the total floor area of the city, 30 out of 81 km^2 (value provided by Agenzia Mobilità Ambiente Territorio of the Municipality of Milan). Figure 1 shows the building units analyzed (grey points) plotted within the municipality boards (blue lines). The results show that the use phase implies the largest contribution to the environmental burdens, with an average of 80% and 60%, considering climate change and the total of the 20 impact categories analyzed, respectively. Vice versa, building construction materials account for 20% and 40% of the entire building stock. When analyzing new constructions (nearly Zero Energy Buildings), the contribution drops to 49% and 46% for the operational phase and rises to 51% and 54% for the construction materials. Of practical relevance, no scientific research has ever been carried out on a plurality of buildings and energy systems at an urban scale. Thus, the research's novelty can also be traced to the innovative outcomes obtained by testing the tool in Milan. For instance, the global warming potential outcomes can be used as benchmark values (i.e., targets, reference, and limits) required by the recast Energy Performance of Buildings Directive (2023). The results for Residential, Commercial, and Retail building units (old and new) are 58, 65, and 84 kg CO_2eq / (m^2 of useful floor area * year), respectively, considering space heating, domestic hot water, and controlled mechanical ventilation. Figure 2 shows the contribution of the EN 15978 Modules evaluated in this research with respect to the "climate change" impact category of the Residential building units. Figure 2a reports the climate profile per year of construction. Figure 2b presents the outcomes per performance energy class. Newly constructed building units have the highest burdens in relation to the highest consumption of building materials as they have to ensure the higher thermophysical performance of the envelope. Likewise, they provide greater benefits from operational energy and reuse, recovery, and recycling potential (Module D). Actions linked with: (i) improving energy systems, (ii) the decarbonization of energy carriers (i.e., electricity and natural gas), (iii) the retrofitting of envelopes, and (iv) low carbon construction materials, are also investigated by running the tool developed. The outcomes obtained were used to verify pieces of legislation listed in the "Fit for 55" and "REPowerEU" for delivering European climate targets. The scenarios lead to the conclusion (for Milan) that the reduction of greenhouse gas emissions by at least 55% (by 2030) is achievable only by retrofitting at a rate of 1.6% per year both energy systems and envelopes, plus also acting on the decarbonization of energy carriers. Figure 3 reports the outcomes related to 4 decarbonization scenarios (i.e., the current scenario in 2022, a short-term scenario in 2030, a base long-term scenario in 2040, and an advanced long-term scenario in 2040). Figure 3a shows the results of 4 energy system technologies: Electric Heat Pumps (EHPs), Gas-absorption Heat Pumps (GHPs), District Heating (DH), and Gas Boilers (GBs). Figure 3b presents the outcomes for building units, considering the whole life cycle.

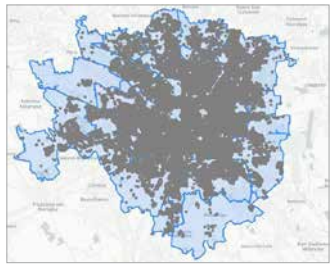

Fig. 1

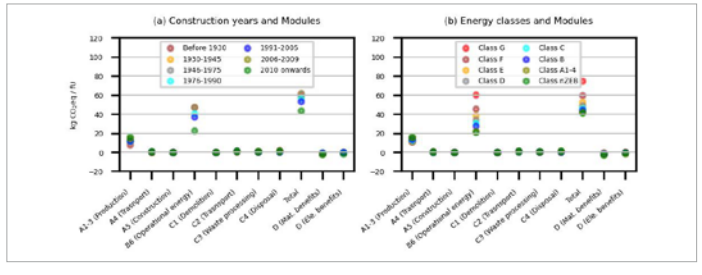

Fig. 2

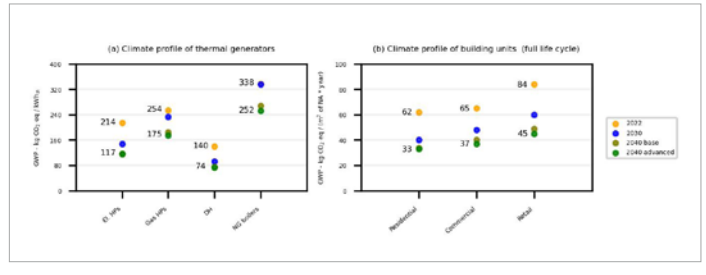

Fig. 3

WET SNOW ACCRETION AND SHEDDING ON OVERHEAD CONDUCTORS

Damiano Fasani - Supervisors: Dr. Federico M. Cernuschi, Prof. Luigi P. M. Colombo
Tutor: Prof. Luigi P. M. Colombo

The present research activity, carried out in collaboration with RSE S.p.A., deals with the issue of snow sleeves accretion and shedding on overhead power lines. During wet snowfalls, the presence of liquid water makes the snowflakes more prone to adhere to the surface of the conductors and ground wires, leading to the growth of heavy wet-snow sleeves on them. This phenomenon poses a serious threat to the infrastructure, as it can lead to the breaking of the wires and to the collapse of the towers. Two numerical models were implemented to predict the snow mass accretion and the evolution of its liquid water content (*lwc*), and the results of the simulations were compared to experimental data collected by RSE in their experimental weather station of Vinadio (CN). The former – the so-called cylindrical sleeve growth model – is a simple and well-established model used to these days to predict snow overloads; the latter – a sectional model based on the works of Poots and Skelton – is more sophisticated and aims at predicting the shape of the snow accretion surface along the span as a function of the wire torsional stiffness. The results showed that both provide similar results for the midspan section in term of accreted mass. A preliminary experimental activity was carried out in RSE Artificial Snow Lab to validate the prediction of the liquid water content as a function of simulated weather variables (wind velocity, air temperature and humidity): it was found that the model underpredicts the rate of change of the *lwc*, since the heat transfer coefficient is underestimated a factor 3.3.
A methodology was defined to measure snow shear and tensile adhesion (i.e., the maximum interfacial stress at failure in shear and normal direction respectively) on different kind of surfaces: particularly, the dependence on surface roughness and liquid water content and the ability of hydrophobic/ice-phobic coatings to reduce wet snow adhesion were investigated.
Shear adhesion was measured by means of a device designed and assembled at Politecnico di Milano (Figure 1), while tensile adhesion was measured in a universal tester using a grabbing system (also in-house designed) based on a Peltier cell-cooled plate (Figure 2).
The results showed a general increase of shear adhesion with roughness and with liquid water content on bare surfaces. Tensile adhesion force on bare surfaces seems to be higher on dry snow, while the corresponding work of separation is significantly lower. Moreover, the adhesion force on wet snow seems to be independent of the actual liquid water content. Coating type greatly affected the adhesive properties: hierarchically textured superhydrophobic treatments were able to reduce wet snow adhesion with respect to the reference case, while SLS slippery coating showed better performances on dry snow, while they were not particularly effective on wet snow. Mechanical tests on snow were carried out to estimate its uniaxial tensile strength using the same grabbing system: ductile-brittle transition as a function of strain rate was observed for dry snow, as also found in the literature. Tests on wet snow showed a reduction in strength with respect to dry snow in the same testing conditions.
The shapes of the failure surfaces were correlated to the value of the "first crack appearance" stress σ_f. It was observed that is maximum at intermediate values of *lwc*, corresponding to a single crack at failure, while decreasing for higher values of *lwc*, with multiple cracks at failure. Despite a certain variety in the failure surfaces, the behavior of wet snow under the tested strain rate is similar to a specific fracture mechanism observed in the literature for dry snow, although at a lower strain rate. This suggest that the brittle-to-ductile transition in wet snow may follow a similar dependence on the strain rates. However, the grabbing system was found to be inadequate for an experimental campaign that covers the lower range of strain rate values, as the freezing plates impose quite stringent conditions on the test duration.
The results of shear adhesion tests were used to establish a simple snow shedding criterion: adhesive failure in a certain cross-section occurs when the average interfacial shear stress reaches the threshold value.
This was integrated into the sectional model in addition to the more "traditional" criterion based on liquid content threshold commonly found in the literature.
The simulations showed the typically observed self-limiting growth (loading-unloading cycles) in the sections near the tower, since shedding is mainly due to the shear stress reaching the limit value. The shear stress criterion is never met at midspan: consequently, continuous growth occurs until the threshold is reached.
A preliminary activity was undertaken using a Finite Elements approach to study the effect of snow time-dependent stress-strain behavior and of a more realistic interfacial stress distribution and how it is affected by snow deformation. A 2D model of the midspan section was implemented, whose results showed that stress concentrate inside the snow sleeve about the cable surface. Snow deformation determines adhesion failure, which in turn, results in an increase of the compressive stress near the top half of the snow-wire interface.

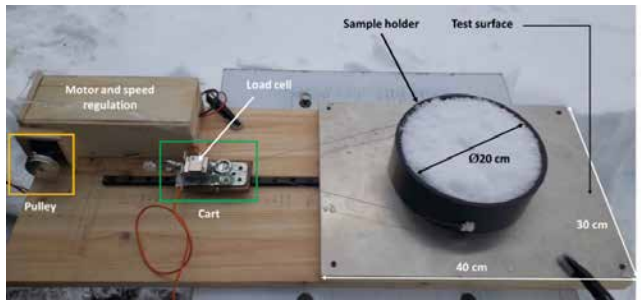

Fig. 1 - Shear adhesion test device

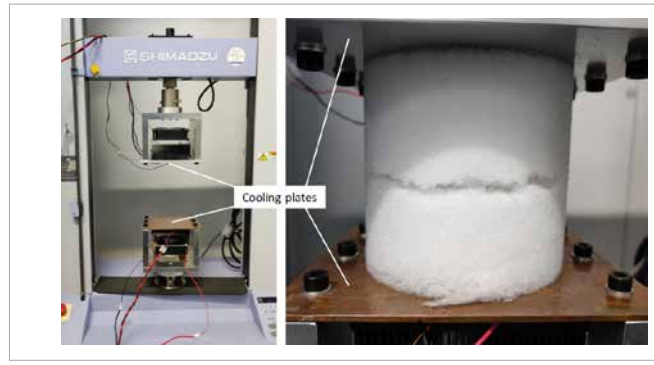

Fig. 2 - Experimental equipment for measuring adhesion strength in the normal direction and snow uniaxial tensile strength. On the left: Material testing machine equipped with cooling devices; on the right: a snow specimen after failure.

MODELLING AND EXPERIMENTAL ANALYSIS OF PEM FUEL CELLS UNDER DYNAMIC REAL-WORLD CONDITIONS FOCUSING ON THE DESIGN OF AN AIR HUMIDIFIER

Amedeo Grimaldi - Supervisors: Prof. Stefano De Antonellis, Prof. Andrea Baricci
Tutor: Prof. Andrea Casalegno

This PhD thesis aimed at investigating and understanding the effect of air humidification on the PEMFC dynamic performance and ageing, through a combined experimental and modelling analysis. A complete 1+1D multiphase non-isothermal dynamic model was, initially, developed and implemented in MATLAB-Simulink environment, integrating the through-the-membrane-electrode-assembly (MEA) model equations with transport equations describing physical behaviour in the along-the-channel direction. Mass and energy transport along cathode and anode gas channels, as well as coolant channels, allowed to simulate realistic conditions that determine significant variations in reactant concentration and temperature in the along-the-channel direction. Exploiting experimental data, based on the ID-FAST driving load cycle protocol, applied on PEM single cell in a four-segment cell testing hardware, it was possible to give a robust validation to the 1+1D model, both at global and local level, thanks to the spatially-resolved information available. The dynamic operation of the PEM single cell was investigated under different operating conditions, demonstrating the optimal prediction capabilities of the model. The obtained results showed the potentiality of the model to capture complex two-phase and non-isothermal transport phenomena both in the along channel and through-the-MEA direction, consistently with a large set of experimental data. The capabilities of the modelling tool were enlarged by developing a new methodology that couples the performance model with PEM fuel cell catalyst durability model, thanks to which it was possible to investigate further the effect of operating conditions on the performance ageing of the PEMFC. Indeed, a new semi-empirical model was developed to estimate ECSA loss under standard voltage cycling, based on the physical mechanisms of Pt catalyst dissolution and redeposition. Combining both the performance model and the catalyst durability model, performance and ECSA losses after one-thousand-hour operation of the reference driving cycle protocol, corresponding to one thousand cycles, were estimated consistently with experimental data, as reported in Figure 1(a). Simulation results proved that most of the performance losses are actually related to the catalyst degradation at a global level during voltage cycling operation. Locally, additional irreversible degradation was observed mainly on the cathode inlet segment, attributable to the degradation of ionomer inside CL. The experimental observations, coupled with model simulations, represent a further step into the definition of the range of operating conditions, conscious of performance and durability issues. Specifically, it was possible to identify the humidification requirements for operating optimally the automotive fuel cell system.

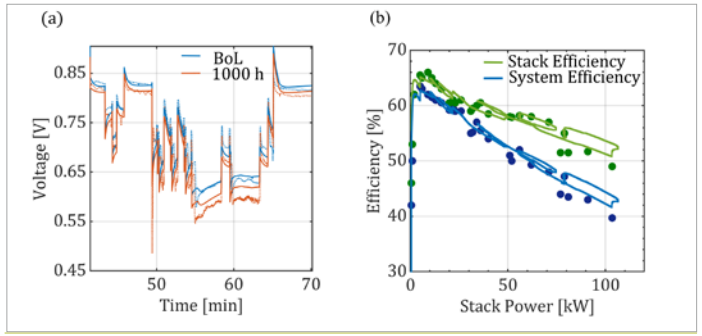

Fig. 1 - (a) Experimental (dotted) and simulated (solid) cell voltage estimated at beginning of life conditions and after 1000 operating hours under driving cycle operation. (b) Experimental (dotted) and simulated (solid) stack and system efficiencies as function of stack power under typical automotive dynamic operation.

Water and thermal management of fuel cell system is influenced strongly by the mutual interaction among PEM fuel cell stack and system components. Specifically, in order to satisfy the aforementioned humidification requirements, analysis of air humidifier technology was performed, looking at the planar-membrane humidifier, focusing both on material properties and design. The thin low equivalent weight PFSA membranes were experimentally investigated, quantifying the vapour-vapour permeation flux and their sorption capacity. The membrane assembly, with 15 μm membrane coupled with the hydrophilic GDL, was found to be the best solution, among the one considered. A further step in the analysis of material properties was done by investigating the effect of channel geometry on water transport, such to obtain the final design of the air humidifier. A small-scale prototype of the humidifier was realized through 3D printing technique. Through a modelling analysis, it was possible to provide a first sizing of the device: a humidifier membrane area equal to 1/12 of the total MEA area was found to properly satisfy the above-mentioned requirements. This result was supported and corroborated by experimental observations, that let to quantify and investigate the steady-state and dynamic performance of the coupling between PEM fuel cell and humidifier. In the last part of the work, the whole fuel cell system model was introduced, in order to understand how the local operating conditions of the stack were influenced by the system operation and its control logics. The model of the balance of plant (BoP) of fuel cell system with the presence of the three main subsystems, namely the cathode air supply subsystem, the hydrogen recirculation loop and the thermal management subsystem, was developed and implemented. Particular attention was devoted to investigate the control logics, trying to mimic the behaviour and dynamics of real fuel cell systems. The experimental database, based on data gathered from testing of a commercial fuel-cell electric vehicle, was used to calibrate and validate the control strategies of system component operation. Both the system and stack efficiencies present a maximum in the load range equal to 5-10 kW, showing a good adherence to experimental data, as reported in Figure 1(b), and maximum efficiency from model simulations is 65% for the stack and 63.5% for the system, against 66% and 63.7%, respectively, from experimental data. PEM stack interaction linked with humidification system, was investigated under the ID-FAST driving cycle protocol, to assess the effectiveness of humidification system and to comprehend further the mutual interaction between those two components and how they are affected by the whole BoP operation. The integration of the designed humidifier inside the whole fuel cell system proved to be capable of satisfying the humidification requirements. Finally, thanks to the whole fuel cell system model framework, an innovative element in the design of the air humidifier was proposed to improve its behaviour under dynamic operation and let to reduce the use of expensive materials, as PFSA membranes. To conclude, the experimental and modelling methodology here developed resulted to be effective in improving the understanding of the local water and thermal management of the PEMFC during its lifetime with state-of-the-art materials. In particular, it led to the identification of critical operating conditions experienced by the fuel cell and to the definition of air humidification requirements, through which it was possible to achieve the proper design of the air humidifier.

DEVELOPMENT AND TECHNO-ECONOMIC ANALYSIS OF BIOMASS-TO-METHANOL PROCESSES

Giorgia Lombardelli - Supervisors: Prof. Manuele Gatti, Prof. Stefano Consonni
Tutor: Prof. Matteo Romano

Bio-Methanol or e-methanol are a promising energy carrier suitable as low-carbon fuel for transportation or as an intermediate in the chemical industry.
This research, based on the combination of modelling and experimental activities, evaluates the technical and economic performance of three alternative thermochemical routes for the production of methanol with low or even negative emissions.
First, results from the experimental tests and numerical calibration of a plug-flow model aimed at describing the kinetic performance of a novel catalyst (developed by Sotacarbo, a research center involved in this project) for MeOH synthesis are presented. The new Cu/Zn/Al/Zr catalyst is characterized under conditions relevant for biomass-derived syngas or CO_2 hydrogenation to MeOH and its performance are compared, from a modelling standpoint, against a commercial catalyst. In order to accurately describe the thermodynamic properties of multicomponent mixtures containing CO_2-H_2-CO-H_2O-CH_4-CH_3OH and involved in the methanol synthesis loop, the binary interaction parameters of the Peng-Robinson thermodynamic model are calibrated starting from publicly available experimental data.
Then, the definition of process designs for the three alternative processes is carried out, each one corresponding to a particular technological pathway: MeOH synthesis throught catalytic hydrogenation of the CO_2 (i) separated from a biogas upgrading unit; methanol synthesis from syngas in biogas-to-MeOH (ii) and biomass-to-MeOH (iii) processes, including a section to adjust the syngas composition via CO_2 removal or H_2 addition from electrolysis (Figure 1).A complete techno-economic analysis (TEA) is conducted, involving numerical modelling and simulation with Aspen Plus for process design purposes, heat and mass balance evaluation at steady state, equipment sizing and costing, and sensitivity analysis assessment. TEA is performed for each technological pathway through the comparison of different process schemes and operating conditions with the aim to identify, under a common framework, the most competitive conversion route in terms of sustainability (from an energy and net fossil CO_2 emissions point of view) and economic feasibility in a full-scale application. A total of 13 full-plant cases have been assessed and different scenarios compared: e.g. condition of the methanol synthesis loop (operating P, Gas Hourly Space Velocity, fraction of purged stream, energy supply mode); strategy to adjust the syngas composition to the stoichiometric module required for maximum MeOH yield (H_2 addition or CO_2 removal); low-pressure versus high-pressure gasification and application of the cryogenic CO_2 removal to the stream fed to the methanol synthesis (with benchmarking against a conventional CO_2 capture technology). Figure 2 shows the Levelized Cost Of Methanol (LCOM) for the following scenarios: CO_2-to-MeOH plants with maximum [1], intermediate [2] and minimum [3] purge fraction and centralized plant [4]; biogas-to-MeOH plants with CO_2 removal upstream [5] and downstream [6] of the reformer, without CO_2 removal [7] and with H_2 addition [8]; biomass-to-MeOH plants with low-P gasification and CCS with MEA absorption [9] or low-T CO_2 removal [10], with high-P gasification and MDEA absorption [11], low-T CO_2 removal [12] or with H_2 addition [13].

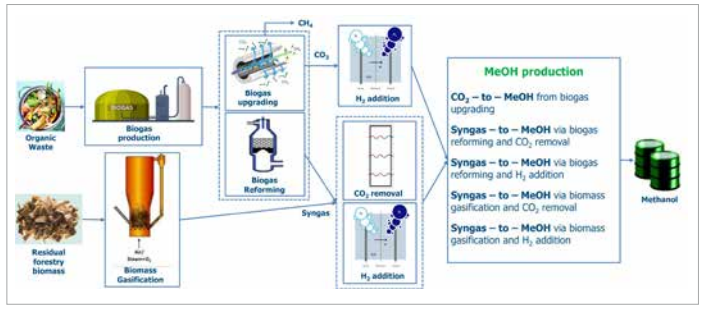

Fig. 1 - The different pathways and configurations of the processes of e- and bio- methanol production analyzed in the present work.

Even though the results among the different route are not fully comparable, due to the different value chains (i.e. type of biomass or residues, plant size and reference energy carrier produced, costs of biomass or residual CO_2 considered), highlight that: biogas reforming is the best approach but it is affected by the competition with incentives on biomethane and it is also strictly influenced by the cost of biogas, while biomass gasification is highly dependent on the scale and cost of the biomass, as well as on need to demonstrate the reliability of pressurized biomass gasification technology and on solving the logistical issues related to the biomass availability and supply chain; lastly, biogenic CO_2 hydrogenation could be an interesting pathway to recover and valorize waste biogenic CO_2 streams but it is not competitive under the present scenario and it may become of interest just when and whether low cost green hydrogen, i.e. of the order of 1 €/kg, will become available.
Results of the CO_2-to-methanol plant report a primary energy efficiency equal to 23%, a net fossil CO_2 emissions of + 3.10 t_{CO2}/t_{MeOH} under the current Italian electricity mix (0.268 t_{CO2}/MWh) and a cost of MeOH of 1363 €/t_{MeOH} in the small scale plant (over 3000 t_{MeOH}/y), reduced to 1130 €/t_{MeOH} in the centralized plant (over 24000 t_{MeOH}/y). Concerning the biomass-to-MeOH scenario, the best option is the pressurized gasification with cryogenic CO_2 removal, reporting a primary energy efficiency around 50%, a negative net fossil CO_2 emissions equal to - 1.66 t_{CO2}/t_{MeOH} and a cost of MeOH of 700 €/t_{MeOH}. When biogas reforming-to-methanol is considered, the most competitive case is the one with upstream CO_2 capture, with a primary energy efficiency of around 60%, a negative net fossil CO_2 emissions equal to - 0.29 t_{CO2}/t_{MeOH} and a cost of MeOH between 299 €/t and 726 €/tMeOH, depending on the biogas production cost (between 0.104 €/Nm³ and 0.42 €/Nm³ in the analyzed case).
All the analyzed scenarios have shown that a carbon tax much greater than current 90 €/t_{CO2} is necessary to make bio- and e-methanol competitive with fossil methanol.

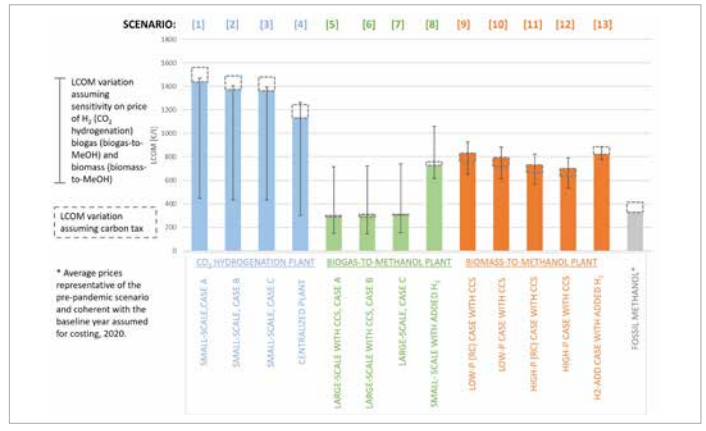

Fig. 2 - Summary of the results in term of LCOM for the 13 analyzed scenarios of CO2 hydrogenation, biogas-to-methanol and biomass-to-methanol plants.

INTEGRATED CALCIUM LOOPING CO2 CAPTURE FOR CEMENT PRODUCTION: FROM PILOT DESIGN AND TESTING TO FULL-SCALE FEASIBILITY

Francesco Magli - Supervisor: Prof. Matteo Romano, Prof. Manuele Gatti

The target of the work is the evaluation of the integrated Calcium Looping (CaL) process for CO_2 capture in the cement industry. This research is pursued in the framework of the Cleanker H2020 project, within which a pilot plant was designed, built, installed, and operated in Buzzi Unicem Vernasca (Piacenza, Italy) cement plant and which eventually demonstrated the technology at Technology Readiness Level 7.

Because of the high share of process emissions, the cement industry looked with increasing interest at Carbon Capture and Storage (CCS) technologies in the last years, which are now widely recognized as an essential lever for the decarbonization of the cement sector and other hard-to-electrify industries.
The Calcium Looping (CaL) CO_2 capture process uses calcium oxide-based sorbents to capture carbon dioxide from the flue gases of a generic emitter.
The process is based on the equilibrium of calcium carbonate ($CaCO_3$) to calcium oxide (CaO) and carbon dioxide (CO_2) at different temperatures and pressures, exploiting the reversible reaction of carbonation/calcination. The calcination heat is provided by burning fuel in pure oxygen, thus producing a CO_2–rich flue gas stream. Calcium Looping can be efficiently integrated into the clinker production process by using cement raw meal instead of pure limestone. In this configuration, the CaL carbonator is integrated in the preheater and treats the rotary kiln gas only, while the CaL calciner coincides with the cement kiln precalciner and a fraction of the calcined raw meal is used as CO_2 sorbent in the carbonator.
The pilot plant is designed to treat up to around 2'000 Nm^3/h of gas in the carbonator (approximately 1.5% of the gas stream produced by the cement kiln), operating with to 4-5 t/h of fresh raw meal (around 3% of kiln capacity). The experimental activity included 5 short test campaigns, with the target of testing many operational conditions, and 4 long test campaigns, with the target of testing for longer periods the most attractive operational windows identified.
The experiments showed that the CO_2 capture efficiency in the carbonator is clearly linked to the temperature measured at the carbonator inlet, which is in turn mainly affected by the solid to gas ratio in the system. The purity of the CO_2 produced is mainly driven by the solid to gas ratio in the system as well, and it is heavily affected by false air leakage.

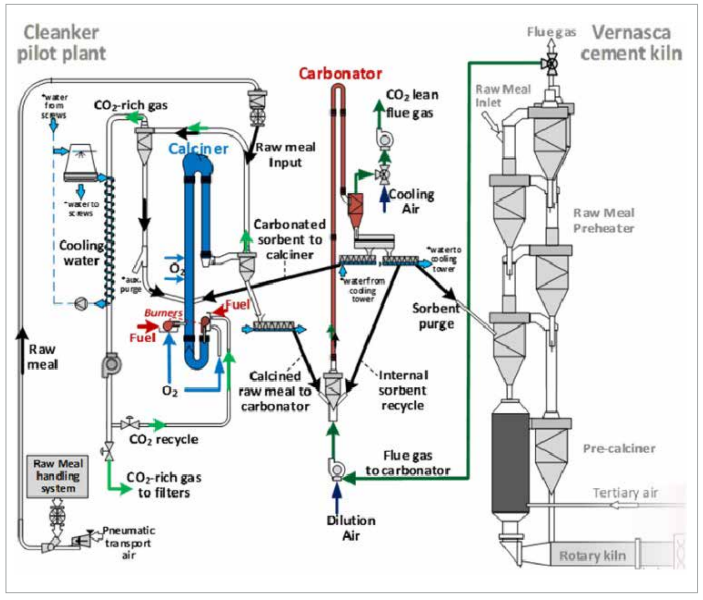

Fig. 1 - Simplified Process Flow Diagram of the Cleanker pilot plant.

The CO_2 Purification Unit (CPU) to be applied downstream the CO_2 capture system has been modeled targeting two different outlet CO_2 specifications and optimized to minimize the incremental clinker production cost. Results show that moderate purity can be achieved with an increased cost of clinker of 16.3 €/t_{clk} (CO_2 recovery 99.3%), while the high purity configuration leads to a 19.3 €/t_{clk} increase (CO_2 recovery 96.1%). Off-design analyses aimed at assessing the impact of air infiltration changing over time highlight the relevance of designing the CPU for the scenario with air infiltrations. For the base case CPU, the cost of clinker increases by 3 €/t_{clk} when moving from zero to 10% air infiltration.

The CPU model has eventually been exploited as one of the simulation bricks to perform the Techno-Economic Assessment of the full-scale application of the integrated Calcium Looping technology to an existing or to a new cement plant (retrofit/greenfield). The direct fuel consumption is increased by 69%/49%, with the greenfield configuration favored by the lower amount of inert recycle gas: however, the direct CO_2 emission reduction is similar, 94 – 95%. On the other hand, the electricity consumption is increased by 30%/52%, leading to Specific Primary Energy Consumption per CO_2 Avoided (SPECCA) of 3.09/2.68 MJ/kg_{CO2}.

In both cases, more than 90% of the Total Plant Cost is linked to 5 equipment units only: the Waste Heat Recovery, the Air Separation Unit, the CPU, the coal mill and the supporting structures. The greenfield case exhibits only slightly lower values compared to the retrofit one in terms of cost of clinker (98.8 vs 102.2 €/t_{clk}) and cost of avoided CO_2 (42.4 vs 45.7 €/t_{CO2}), mainly due to the lower thermal energy demand.

PLASMONIC AND MULTIFUNCTIONAL NANOSTRUCTURED METAMATERIALS WITH TAILORED ELECTRICAL AND OPTICAL PROPERTIES

Cristina Mancarella - Supervisor: Prof. Andrea Li Bassi

Very recently, a myriad of strategies have been explored to pursue the striving need for enhancing efficiency of solar-driven energy conversion processes, enabling the harness of light across the entire solar spectrum (from visible VIS to infrared IR). In this perspective, plasmonics is an intriguing field because it allows an ultra-fine tailoring of light-matter interactions, starting from the nanoscale. These goals can be reached by exploiting plasmon resonances, known as light-driven collective oscillations of conduction electrons due to the resonant interaction with electromagnetic radiation. Plasmonic excitations have stood at the forefront of nanotechnology for decades, owing to the ultra-high intensification of light-matter interactions that they can boost. At present, noble metals (e.g. Au) are dominant in the field and the far most employed due to their high-quality resonances in the visible (VIS) range. However, the intrinsic limitations in modulating plasmons beyond optical frequencies, as imposed by the constrain of a fixed electronic carrier density, have stimulated a dramatic and urgent quest for novel and revolutionary plasmonic materials. In this context, transition metal nitrides (e.g. TiN) have grown as promising contenders to conventional metals, offering cost-effectiveness, thermal stability, Complementary Metal-Oxide Semiconductor (CMOS) integrability and modifiable plasmonic responses across VISnearIR (NIR) window by manipulating composition and stoichiometry. Concurrently, oxynitrides are rising interest as well, due to the unique capability to cross twice the zero value of the real permittivity ϵ_1 in a wide spectral range, resulting in a Double Epsilon-Near-Zero (D-ENZ) character at which new exotic phenomena arise, namely multiple resonances, enhanced optical non-linearities or improved photocatalytic activity. Conversely, Transparent Conductive Oxides (TCOs, Ta-doped TiO_2) possess tunable carrier density, thus are promising for extending the plasmonic features up to the infrared (IR) domain. Within this exciting panorama, scientific attention has gravitated on meta-structures based on alternative materials that can potentially supply broad multifunctionalities, to simultaneously address various requirements suitable for specific needs in energy, optoelectronics, biosensing and nano-photonics. Indeed, the metamaterial approach stands as one of the most straightforward mean through which plasmonic features of established media can be spectrally tailored in wider frequency regions, with the possibility to activate unexpected functionalities. Specifically, architectures called Hyperbolic Metamaterials (HMMs) show an anisotropic permittivity ϵ (parallel and perpendicular components to the multilayer surface) due to the periodic alternation of conductors ($\epsilon_1 < 0$) and dielectrics ($\epsilon_1 > 0$). The hyperbolic region enables the propagation of unique high-k waves, activating, for instance, unprecedented light manipulation. My PhD focused on the experimental realization and characterization of nanocomposites and multilayer metamaterials through an innovative approach, merging traditional metals (e.g. Au nanoparticles), and alternative plasmonic candidates (nitrides, TCOs) via original design strategies. The final goal was to advance the knowledge of alternative materials used, alone or in combination, with the future mission to substitute, at least partially, traditional metals causing fabrication issues and lacking in optical tunability, major limitations inhibiting practical implementation of plasmonic technologies in next-generation electronic and nanophotonic devices. The primary short-term objective was to prove the feasibility in production of metamaterials, e.g. HMMs, employing alternatives plasmonic media and unveil material responses arising from the unconventional coupling of materials and properties (transparency, conductivity, tunable VIS-IR plasmonics, active modulation). The main fabrication technique adopted is Pulsed Laser Deposition (PLD), selected for its versatility in tailoring the aforementioned materials characteristics by managing deposition parameters as necessitates. Systems investigated comprehend nanocomposites with Au NPs integrated in Ta-doped TiO_2 TCO, fully-based Ta-doped TiO_2 TCO conducting and transparent multilayers, TiN-based multilayers and novel plasmonic titanium oxynitrides TiO_xN_y. Indeed, Au-TCO nanocomposites, where NPs are placed at film-substrate interface or within the film itself (Figure 1a) show wide tunability of Au plasmonic resonance achieved by carrier concentration control (Figure 1b), while keeping transparency and conductivity, to be applied in plasmonic functionalized electrodes. Ta-doped TiO_2 multilayers (e.g. compact/porous) have been fabricated straightforward with an ingenious approach by exploiting PLD synthesis, able to vary the optoelectronic features of single layers starting from the same material (fixed doping, 5% or 10% of at. Ta). Active-tunable photonic crystals can be realized in this way (Figure 1c). Indeed, by applying low voltages (up to 7 V), the photonic band gap can be blue-shifted of 11-14 nm solely by exploiting the carrier concentration modulation of the TCO layers (Figure 1d), in a solid-state device without using liquid electrolyte, intrinsically posing environmental concerns and fabrication issues. In addition, a remarkable advancement has been pursued regarding the assessment of plasmonic characteristics of Ta-doped TiO_2 films in the IR, fundamental platform for future design of HMM in this peculiar spectral region. TiN-based multilayers have been realized (Figure 2a) and proved to theoretically show wide hyperbolic behaviour in VIS-NIR (Figure 2b), while the challenging synthesis of TiO_xN_y (Figure 2c) showing D-ENZ has been successfully addressed by controlling deposition parameters (Figure 2d). Despite the variety of structures and properties inspected, the common fundamental denominator is the tunability of the spectral window of plasmonic outputs spanning from VIS to IR, along with diversified functionalities merged at once, cross-disciplinary attitude, and feasibility in fabrication. The list of practical applications includes, but is not limited to, plasmon-functionalized transparent electrodes, biosensors from VIS to IR, optoelectronic elements and metamaterials for thermal energy or colour manipulation, anti-counterfeiting technologies and thermo-photovoltaic emitters.

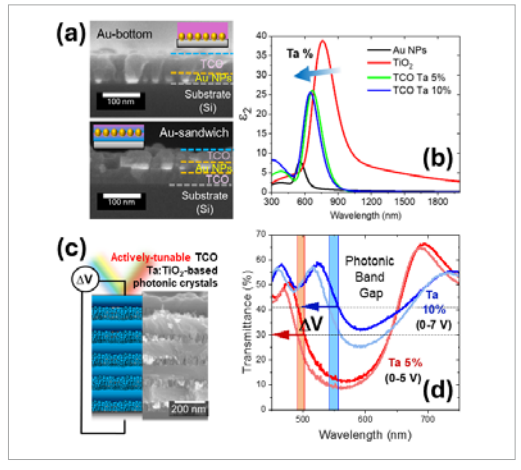

Fig. 1 - (a) SEM images of Au-TCO nanocomposites and (b) blue-shift of the peak in the imaginary part of the dielectric function (associated to Au plasmonic resonance) according to the Ta doping. (c) Scheme and SEM image of Ta:TiO_2-based active-tunable PCs, with the resulting blue-shift in the photonic band gap (d) after application of an external bias.

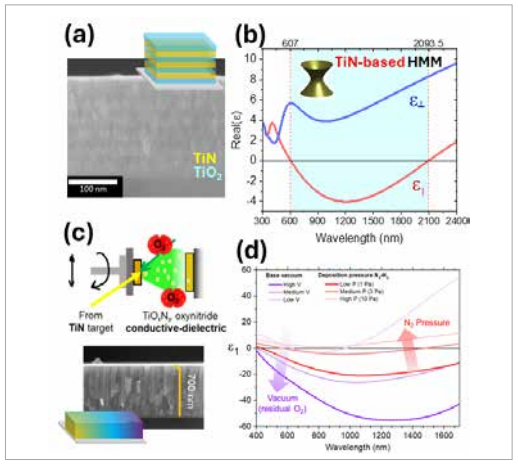

Fig. 2 - (a) SEM image of TiN-TiO_2 multilayer; (b) wavelength region in VIS-NIR of HMM behavior predicted from the plot of simulated anisotropic $\bar{\epsilon}$ of the multilayer (parallel and perpendicular components); (c) TiN-oxynitride SEM image and ϵ_1 plot (d) showing the tunability of D-ENZ behaviour according to deposition parameters.

CARBON ATOMIC WIRES: FROM THEIR SYNTHESIS TO THE COMPREHENSION OF THEIR UNIQUE VIBRATIONAL AND ELECTRONIC PROPERTIES

Pietro Marabotti - Supervisor: Prof. Carlo Spartaco Casari

Carbon atomic wires (CAWs) represent fascinating linear sp-carbon chains with unique structural and electronic properties, making them highly promising for a wide array of technological applications. CAWs are the finite realization of carbyne, the ideal infinite sp carbon allotrope, and have two possible isomers: polyynes are large-bandgap semiconductors (or insulators) made of alternating triple and single carbon bonds, while cumulenes can be considered small-bandgap semiconductors composed of a sequence of equalized double bonds. These molecular systems have been scarcely investigated in the past, due to their poor stability and low synthesis yield.
The primary focus of this thesis revolves around harnessing the potential of pulsed laser ablation in liquid (PLAL) to synthesize polyynes with variable terminations and properties across a diverse spectrum of organic solvents. Through meticulous optimization of the ablation parameters, I have succeeded in enhancing the PLAL synthesis yield, while simultaneously standardizing a precise method to assess the formation efficiency and conducting exhaustive investigations into the impact of solvent and target properties on polyynes formation. Remarkably findings include the discovery of novel halogen-capped polyynes through ablation in halogenated organic solvents, further expanding the possibility of functionalizing CAWs by PLAL.
A significant portion of this work has been devoted to the extensive utilization of infrared and Raman spectroscopy techniques, allowing for a comprehensive exploration of CAWs' properties in both PLAL-produced samples and stable, chemically synthesized powder samples provided by external collaborators. Exploiting the tunability of synchrotron radiation in the UV range where polyynes feature sharp and intense vibronic absorption progressions, UV resonance Raman spectroscopy has provided invaluable insights into the intricate relationship between the structural, vibrational, and optoelectronic properties of polyynes, uncovering intriguing size-dependent electron-phonon coupling and vibrational anharmonicity.
Additionally, in situ Raman spectroscopy investigations have delved into the behavior of cumulenes within electrochemical cells, emulating their behavior in prototypal sp-based field-effect transistors. Noteworthy results have been obtained by developing innovative in situ probes based on surface-enhanced Raman scattering and UV resonance Raman spectroscopy. These probes have contributed significantly to elucidating the elusive growth mechanisms underlying polyynes' synthesis via PLAL, unveiling unique formation-degradation fast processes governing the final products of ablation experiments.
Through this comprehensive and multidisciplinary approach, this thesis aims to establish a deeper understanding of CAWs' synthesis and properties, thereby facilitating enhanced control over their formation, functionalization, and eventual utilization in various molecular optoelectronic and energy conversion devices, thereby paving the way for groundbreaking advancements in the field.

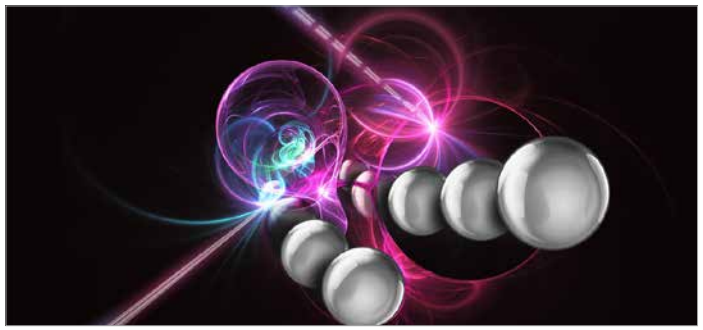

Fig. 1 - Pictorial representation of the in situ experiment conducted during pulsed laser ablation in liquid. The graphite target (black disk) is ablated by the pulsed laser (dashed beam) providing carbon chains. The chains are probed by synchrotron-based UV-radiation (continuous beam), representing the in situ probe that allowed us to monitor the growth of polyynes by PLAL.

DEVELOPMENT OF INNOVATIVE TRANSCRITICAL POWER CYCLES WORKING WITH CO2 MIXTURES FOR CONCENTRATED SOLAR POWER APPLICATIONS

Ettore Morosini - Supervisors: Prof. Giampaolo Manzolini, Prof.Gioele Di Marcoberardino

Context and scope

The thesis focuses on the adoption of CO_2-based mixtures as innovative working fluids for high temperature transcritical power cycles, with a focus of the application in concentrated solar power plants (CSP).
With respect to supercritical cycles with pure CO_2 (sCO_2), mixtures can be adopted to increase the critical temperature of the working fluid, above 70°C. This way it becomes possible to adopt a pump within the power cycle, replacing the supercritical compressor: an advantageous modification for air-cooled cycles located in relatively high ambient temperatures environments (as in CSP applications), both from an efficiency and an operational perspective.
Within the work, equations of states for mixtures are carefully adopted, especially detailing the two-phase region, during working fluid condensation. Moreover, significant attention is given to address the modeling of all the plant components, both of the CSP sub-system and of the power cycle, with dedicated 1D tools, able to predict the system performance both at design and off-design.

Methods and procedure for the power cycle simulations

At first, the thesis objective is to characterize from a thermodynamic perspective the behavior of a few innovative mixtures identified for the first time in literature. To do so, both cubic and advanced equations of state, with the computed binary interaction parameters, are used to fit at best the computed thermodynamic variables of the mixture with the available experimental data. For the CO_2+C_6F_6 and the CO_2+$SiCl_4$ mixtures, as no data were found in literature, an experimental campaign was carried out, within the thesis, measuring the VLE and the density of the mixtures.

Once the thermodynamic of the mixture is numerically modelled, the performances of the cycles are simulated within AspenPlus, according to the maximum temperature allowable by the working fluid, determined by the thermal stability of the CO_2-dopant (between 550°C and 700°C). All the selected cycle configurations (a combination of plant layout, maximum temperature, and mixture composition) are found to outperform the performance of sCO_2 cycles at same boundary conditions, leading to an increment of power produced between 2% and 5%.
After introducing few CO_2-based mixtures and their promising performances in power cycles, a wide analysis on the cycle components is proposed, focusing on heat exchangers (HX). Detailed finite-volumes models are developed in MATLAB and presented for the recuperator, the primary HX and the condenser of the CO_2-based cycles. The innovative narrative of the thesis exploits models for the convective heat transfer coefficients and pressure losses of binary mixtures, evidencing the results in particular during the mixture condensation. By comparing different design for all the HX of the cycles, it is understood that no penalization of the heat transfer coefficients and HX area can be foreseen for components with CO_2 mixtures with respect to pure CO_2, confirming the promising features of CO_2 mixtures.

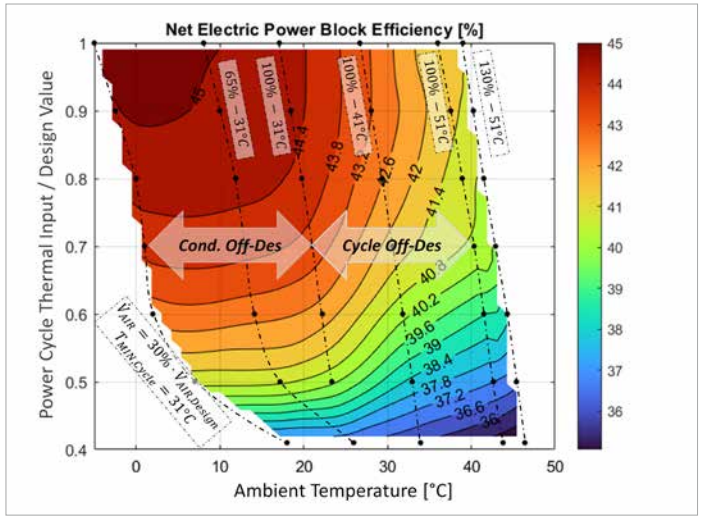

Fig. 1 - Performance in off-design of a simple recuperative CO2-based mixture power cycle for state-of-the-art CSP applications

Methods and results of the innovative cycles in CSP environments

As the cycles and the design of the HX are fully defined, the work focuses on the simulation of solar tower CSP plants. Validated literature models are adopted to simulate the heliostat fields, the thermal performance of the receivers and the auxiliary systems, both at design and off-design conditions. A comprehensive sensitivity analysis is developed to optimize, for each solar plant proposed (varying the heat transfer fluid, receiver geometry and storage medium), the best configuration of CO_2-mixture transcritical cycles from a techno-economical point of view through an annual analysis estimated on an hourly basis, by minimizing the computed LCOE. Results underlines that, differently from pure sCO_2 that is suggested in literature predominantly for next generation CSP plants (with maximum temperature of 700°C), CO_2-based mixtures with fluorocarbons (such as CO_2+C_6F_6 or CO_2+C_4F_8) exhibits the best performances even with maximum temperatures coherent with the state-of-the-art of the steam-based CSP plants (550°C), suggesting the hypothetical repowering of already existing plants.

Accordingly, the thesis points to innovative solutions not investigated before both in terms of working fluids and methodologies for the cycle analysis: the proposed power cycles with CO_2-mixtures are found as an effective solution for any high-temperature applications such as CSP, nuclear or high temperature waste heat, and not yet competitive at lower temperatures.

Methods and results of the cycles in off-design conditions

To conclude the thesis and fully determine the potentialities of the innovative cycles, a methodology for the calculation of the cycle in off-design is established. The iterative procedure developed in MATLAB adopts all the finite-volume models of HX developed, including an analysis on the off-design behavior of the turbine, and it runs calculations both at variable thermal input and variable ambient temperature for the whole power cycle. All the plant components are simulated in off-design, including the CSP plant and its subsystems, operating the power block in sliding pressure and the turbine in full admission, by modifying the rotational speed of the air-condenser fans to match the variable cooling demand. Results show, for the simple recuperative cycle operating with the CO_2+C_6F_6 mixture at 550°C of maximum temperature, net electric efficiencies in CSP plants between 44%-42% at full load (overperforming the state-of-the-art steam cycle by 5% in relative terms and increasing the flexibility of the system due to the cycle compactness), and 40% at loads below 50%. Further studies will be required for the identification of additional CO_2-dopants for very high temperatures (above 600°C) and for the simulation of the cycle transient behavior, following the fast and variable load demand of the grid.

CHARGE TRANSPORT IN PRINTABLE CARBON-BASED SEMICONDUCTORS FROM SP2-CONJUGATED MATERIALS TO SP-CARBON WIRES

Stefano Pecorario - Supervisor: Dr. Mario Caironi

Tutor: Prof. Carlo Spartaco Casari

Solution processable organic semiconductors and semiconducting single-walled carbon nanotubes (SWCNTs) are at the heart of the emerging field of printed electronics. Flexible electronic circuits, wearable biosensors, semi-transparent solar panels, edible electronics and neuromorphic devices are only a few examples of the innovative applications made possible by the unique optoelectronic and mechanical properties of carbon-based semiconductors. Still, boosting charge transport in solution processed carbon-based semiconductors is necessary to compete with the electrical performance offered by inorganic semiconductors. In order to design organic semiconductors with enhanced charge mobility and functionalities, it is crucial to understand relationships between electrical and structural properties from the molecular level up to the macro-scale. Likewise in solution processed random networks of semiconducting SWCNT, understanding the effects of the network composition on charge transport is important to establish efficient processing standards leading to high-performance devices.

This thesis aims to shed light on the structure-property relationships in field-effect transistors based on thin films of three classes of printable semiconductors. The first study regards the effects of molecular encapsulation on the photophysical and charge transport properties of a high-mobility semiconducting polymer, PNDIT2, which is widely employed in n-type organic field effect transistors (OFETs) and as non-fullerene acceptor in organic photovoltaics.[1] Encapsulating macrocycles are covalently bonded to the thiophene units, while the naphthalenediimide (NDI) moieties are free to establish intermolecular interactions. Molecular encapsulation emerges as a promising approach to enforce planarization of the polymer backbone and to avoid coiling of the polymer chains in solution. Furthermore, the encapsulating rings promote crystalline packing through an intermolecular-lock mechanism. Due to the presence of the macrocycles the π-π stacking distance between NDI units increases with respect to the naked polymer, which is reflected in lower charge carriers mobility. Still, charge transport is remarkably preserved in the encapsulated PNDIT2, as demonstrated by ideal OFETs characteristics.

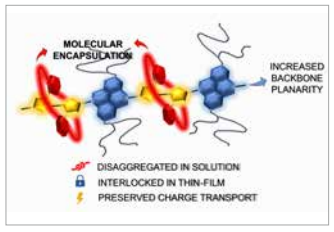

Fig. 1 - Effects of molecular encapsulation on the photophysical and charge transport properties of a high-mobility semiconducting polymer PNDIT2 (from Ref. 1).

The second part of the thesis examines charge transport in field-effect transistors based on solution processed random networks of single-walled carbon nanotubes (SWCNTs). Monochiral (6,5) SWCNT networks and multichiral networks containing five different semiconducting species with different band gaps are investigated by charge modulation microscopy (CMM). CMM allows to map charge-induced optical features in the transistors channel with micrometric resolution. Hence, it is possible to visualize the distribution of the free carriers and identify correlations with local properties of the network, such as SWCNTs density and species composition. The CMM maps provide direct evidence that holes and electrons are transported preferentially through the same percolation paths.

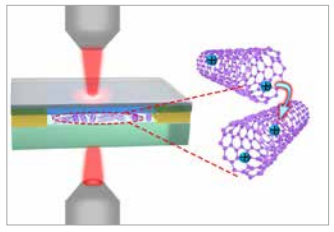

Fig. 2 - Charge transport investigation in semiconducting carbon nanotubes networks by charge modulation microscopy (from Ref. 2)

A dependence of the charge-modulated signal on the density of SWCNTs is observed for the monochiral network during the switching of the transistor. Moreover, it is found that the monochiral network presents less fragmented percolation pathways with respect to the multichiral network, which is in good agreement with the better performance of devices based on monochiral SWCNT.

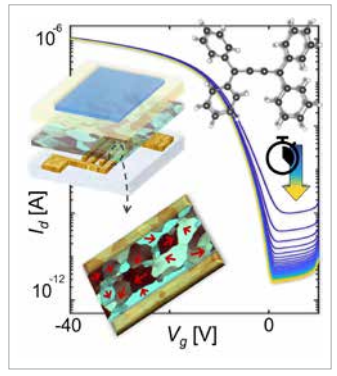

Fig. 3 - Stable and solution-processable cumulenic sp-carbon wires with record mobility of 0.1 cm2/Vs in organic field-effect transistors (from Ref.3)

Finally, molecules based on a linear backbone of sp-hybridized carbon atoms, namely cumulenic sp-carbon wires, are introduced as a novel class of conjugated semiconductors for organic electronics. Solution-processed thin films of tetraphenyl[3] cumulene ([3]Ph) are deposited by a large-area meniscus-coating technique, and employed as active layers in OFETs. Optimized polycrystalline thin films of [3]Ph show ideal field-effect characteristics and hole mobility up to 0.1 $cm^2 V^{-1} s^{-1}$. Moreover, the devices display promising operational stability in air without specific encapsulation. A comprehensive spectroscopic and structural characterization, combined with DFT calculations, allow to correlate optical absorption features and charge transport properties with the thin film microstructure, thus providing guidelines for the molecular design of a whole new family of performant organic semiconductors with sp-hybridized backbone.

A CALIBRATED MODEL FOR THE PREDICTION OF THE ELECTRICAL BEHAVIOUR OF BIPV MODULES WITH OPTIMIZED COLOURED FRONT GLASS PANE

Martina Pelle - Supervisors: Prof. Francesco Causone, Dr. Laura Maturi

Tutor: Prof. Livio Mazzarella

Recent studies have reported that achieving the complete decarbonization of the Italian electricity system by 2030, while ensuring national power self-sufficiency at the lowest possible cost, would require the installation of approximately 200 GW of solar power, which corresponds to about 1200 km^2 of installed PV modules. Harvesting solar energy by exploiting building surfaces can help to promote on-site renewable energy production and increase self-consumption and it will contribute to achieving the targets for the penetration of renewable energy in the country's energy mix (as in the case of European Member States), while reducing the need for land allocation for solar farms.

Building integrated photovoltaics (BIPV) represents a viable technical solution to incorporate renewable energy production in the built environment, exploiting the solar potential of buildings' surfaces by integrating photovoltaic (PV) systems into the building envelope. BIPV systems are active envelope components, both for façades and roofs, with a dual function: they serve as both a building envelope and as a power generation system, harvesting solar energy for on-site energy production. Despite this high potential, up to now the large-scale application of BIPVs has been hampered due to the narrow variability typical of the standard PV modules.

The introduction of coloured BIPV modules has been game-changing for BIPV applications, whose aesthetic has been enhanced by concealing or modifying the visual perception of the original material of the PV cells through coloured layers that make the modules' appearance mimics the standard construction products, to the detriment of the module's power conversion efficiency and increase in costs. Therefore, even though highly customizable BIPV technologies offer greater aesthetic possibilities and flexibility in architectural design, customization could also present a limitation for the industrial production and cost reduction of BIPV technologies.

The activities conducted in this study were designed to evaluate in depth the performance of customised BIPV products, with a particular emphasis on the impact of aesthetics on energy performance in coloured BIPV technologies.

The first result of the research has been the development of an interdisciplinary and multilevel methodological framework for the performance assessment of customised BIPV products, which integrates aesthetic and technical aspects. On these bases, an evaluation matrix has been defined, which is intended as a decision support tool for the selection of BIPV technologies for a specific application. Furthermore, the developed methodology brought to the identification of hidden coloured BIPV technologies as the ones providing the highest customization potential but also a knowledge gap, regarding the relation between aesthetics and energy-related performance in coloured BIPVs.

Therefore, the second part of the research focused on the development of a model for assessing the performance of coloured BIPV technologies that incorporate translucent front glass panes to conceal c-Si solar cells from the user's view. The novelty of this activity lies in the capability of the model to assess at the same time (i) the highest possible PV efficiency for a module that reproduces a specific colour and (ii) the colour formulation that allows obtaining such maximum power output. The model development consisted of three main parts: 1) an experimental campaign, to collect the data required as the model's input, which contributes also to build-up a database including (i) primary ceramic-coated glass panes' spectral properties and (ii) detailed electric performance of coloured BIPV, both data currently scarce in the literature; 2) the development of an optimization algorithm able to detect (i) the highest possible PV efficiency for a module that reproduces a specific colour and (ii) the colour formulation that allows obtaining such maximum power output; 3) the model calibration for six arbitrarily chosen colours. The model was applied to six colours, and for four cases out of six, it provided optimized coloured glass panes with higher power conversion efficiency (+ 3%), compared to the target. Therefore, one of the main results of the developed model is the possibility to detect the spectral features of an optimized coloured glass pane, whose colour composition provides a similar colour sensation compared to the target, and the maximum possible module's efficiency for the selected colour and technology.

The developed model is intended to support BIPV module manufacturers in the development of customized products able to balance aesthetic and energy aspects, allowing them to evaluate the impact of the coloured layer on the electric output without producing and testing prototypes. This tool can contribute to decreasing the cost of coloured BIPV products, by facilitating mass production while preserving the customization potential, thereby allowing to optimize the product performance. Furthermore, it would provide designers and final users with reliable information for more conscious design choices, that balance energy and aesthetic aspects.

NEW BIOFUELS FOR MOBILITY: TECHNO-ECONOMIC ANALYSIS AND REACTOR MODELLING FOR A BIOGAS TO METHANOL PROCESS

Riccardo Rinaldi - Supervisors: Prof. Matteo Romano, Prof. Carlo Visconti

INTRODUCTION

This Doctoral Thesis deals with a techno-economic assessment of methanol (MeOH) production from biogas, with the goal to carry out a comparison among three different process configurations and assess the effect of process parameters on the plant performances. The flexible integration with an electrolyzer that compensates the feedstock CO_2 excess is also accounted.
In view of the small-scale MeOH synthesis, the limits of the traditional multi-tubular reactor technologies for MeOH synthesis are assessed and the possibility of utilizing innovative reactors for MeOH synthesis is studied.

PLANT ANALYSIS

The process converts 4074 kg/h of biogas to MeOH and consists of three main sections: removal of contaminant species and excess CO_2, reforming, MeOH synthesis and purification. A block flow diagram of the process is represented in Figure 1.
Three options are envisaged for CO_2 removal: (i) upstream or (ii) downstream of the reforming section, or (iii) no CO_2 removal. In the last case, MeOH synthesis does not take place in stoichiometric conditions.
The three configurations are compared in terms of process and economic key performance indicators: MeOH mass flow rate, fixed capital investment (FCI), net present value (NPV), and levelized cost of methanol (LCOM). MeOH production is higher in the Upstream separation case (2480 kg/h), while it has the lowest value (2403 kg/h) when no CO_2 separation is performed. The economic analysis confirms that the Upstream separation case is the most remunerative among the studied process configurations. The worst economic performances are obtained in the Downstream separation case, penalized by low MeOH productivity (2433 kg/h) and elevated capital expenditures (FCI is 12.2 M€), while, when no CO_2 separation is carried out, the fixed capital investment is the smallest but the NPV is lower than that of the Upstream case (9.3 M€ vs. 9.8 M€ of the Upstream case) and LCOM higher (379.3 €/t vs. 378 €/t). A sensitivity analysis on several process parameters is carried out on the Upstream case (i.e., the most profitable). The parameters varied are the recycle ratio (RR, in the range 3-7), methanol reactor operating pressure (p_{MeOH}, 50 bar - 95 bar), and gas hourly space velocity (GHSV). While the recycle ratio and the GHSV variation have a marginal effect on the process performances, greater profits are earned at lower pressures, due to reduced compression costs. The 50 bar Upstream case is thus selected as the best-case scenario.

PROCESS FLEXIBILITY

In order to fully exploit the feedstock carbon content, the intermittent use of the excess CO_2, together with renewable green H_2, is studied to increase MeOH production. The goal is to assess the impacts of the two working conditions, i.e., with and without extra H_2 (25 mol/s - 100 mol/s) and CO_2 (8 mol/s - 32 mol/s) on MeOH productivity, temperature profiles, and transient behavior of the reactor.

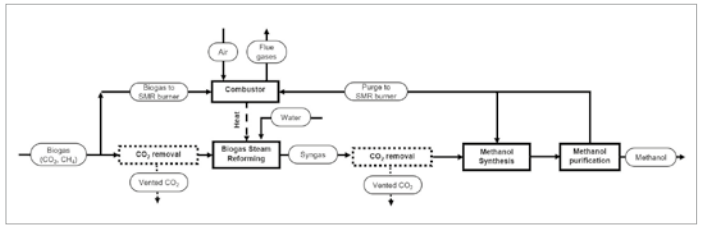

Fig. 1 - Simplified scheme for the biogas to MeOH process.

H_2 and CO_2 addition leads to a boost of produced MeOH, that goes from 21.5 mol/s when no extra H_2 and CO_2 are used, to 41.1 mol/s, with 100 mol/s of H_2 and 32 mol/s of CO_2. Despite being beneficial for the system, the higher flowrate leads to a greater distance from the chemical equilibrium: this requires an increase of unconverted gases recirculation. In view of a compact – scale process, the possibility of reducing the tubes length or the number is analyzed. In the former case, methanol production is subjected to moderate losses but high temperature hotspots (the selectivity limit of 540 K is reached when ¼ of the original tube length is adopted); in the latter, the temperature is always under control, but the quantity of produced methanol decreases more steeply (-5.9% when only ¼ of the tubes are employed). Any further reduction of reactor dimension is not possible by means of packed beds, due to the worsening of the convective heat transfer. A viable alternative could be the use of novel chemical reactor design.

ALTERNATIVE REACTOR DESIGN

The solution proposed for small-scale synthesis is the adoption of a pillow-plate geometry for MeOH reactor, i.e., a unit with a pillow-like structure that can improve heat and mass transfer across the catalytic bed, as reported in Figure 2.
The pillow-plate unit performances are assessed and compared to those of a traditional packed bed at different reactor axial lengths (6 m – 1 m) through a validated Computational Fluid Dynamics (CFD) approach. The analysis proves that multi-tubular reactors are affected by poor convective heat transfer that leads to very low reactants conversions and excessive thermal apices. The use of pillow-plate reactors, conversely, allows for an effective small-scale MeOH production, due to a very effective heat transfer. When 6 m long reactors are utilized, for instance, the model predicts rapid temperature augmentation (almost 50 K in less than 0.3 m) for the pillow-plate reactor, whereas the increase is remarkably more gradual in the case of the packed bed unit (50 K increment in 0.85 m). These conditions exacerbate upon shortening reactors tubes: when 1 m long units are employed, the packed bed reactor achieves the highest temperature, with a model prediction at the reactor exit of 557 K, while the pillow-plate unit shows a thermal peak at 537 K. Moreover, while methanol production decreases when short multi-tubular reactors are utilized, this trend is not observed with the pillow-plate arrangement, as the molar composition is always close to the chemical equilibrium. Pillow-plate reactors thus prove to be a viable possibility for compact-scale methanol production from biogas.

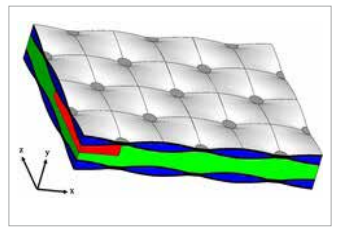

Fig. 2 - Sketch of pillow-plate reactor.

ENERGY PROTOCOL FOR SIZING, PLANNING AND OPERATION OF THE 3RD GENERATION MINI-GRID IN SUB-SAHARAN AFRICA

Castro António Soares - Supervisor: Prof. Emanuela Colombo

Sub-Saharan Africa (SSA) is the region with the highest rate of people living without access to electricity in the world. In 2019, the region registered around 620 million people deprived of access to electricity, but this number was expected to decrease over time due to the SDG 7 goal. For instance, in Mozambique, only 38% of the population has access to electricity and the majority population is living in rural areas in extreme poverty caused by lack of electricity, lack of income, education, and healthcare. SSA is a region endowed with untapped and inexhaustible energy resources. Nevertheless, mini-grids are not a new phenomenon, for almost more than 25 years, public services have owned and operated off-grid diesel generators for remote villages. Therefore, energy development is increasing in the region, although it is not fast enough, because of a set of barriers that are undermining the development of the mini-grids in rural settlements, such as Energy Policy and Regulatory barriers, Economic and financial barriers, technological and human resources barriers, social and geographical barriers**,** and some other challenges. The lack of clear and effective energy policy and regulatory framework are the main barriers. Therefore, the creation of an energy protocol will spur the energy sector to use it as a guideline for third-generation mini-grid development and will be used by other institutions such as the private sector, NGOs, partners, academics, policymakers, and others. In addition, according to World Bank, it is necessary to keep striving to reach SDG 7 goal and develop studies related to third-generation mini-grid systems using renewable energy resources to tackle the energy crisis in SSA. This research analyzes different mini-grid problems in the region and will focus on the systems deployed in Mozambique as a case study. The required data were collected considering four different mini-grids belonging to FUNAE FP, addressing various kinds of problems, such as I)- Oversized and undersized mini-grids; ii)- Mini-grid without backup system and works less than 24h; iii)- Low power generation to meet demand; iv)- Frequent mini-grid shutdown; v)- Lack of standard model and effective mini-grid deployment and management process**.** By analyzing the case study, it is expected to deeply understand the issues that trigger these problems, why these issues arose, to identify desirable or possible solutions using the theory/experience suggested by the research and learn a lesson from it, and required actions to propose improvements, to present a realistic implementation plan, and present viable recommendations. This study considers five different case studies addressing all the above-mentioned problems in Ndoro village, Garagua mini-grid, Chissinguana mini-grid, Mecula mini-grid, and Muôha mini-hydropower, and properly considered the challenges of each mini-grid which need to be addressed are as follows: In **Mecula Village** the system is oversized, while in **Chissinguana Village** the mini-grid was installed without diesel generator as a backup system (undersized), in **Garagua village** the system was installed properly but it has frequent shutdown problem (undersized), and in **Muôha village** the system was deployed without a backup diesel generator, battery bank, and has one source of power generation (water - river). Apart from the above-mentioned case studies, a case study in Sofala Province where there is a small community in ***Ndoro Village*** with ***19,161*** people living deprived of electricity. To meet SGD 7 goal, is intended to develop a study from scratch to propose a model for the installation of a mini-grid system in the area.

From scientific literature is very difficult to find cases in which all these challenges and barriers are discussed together. This study took into consideration all these aspects and will also help to bridge the existing gap in grey literature, as it is also necessary for those who are doing this work in the field such as the Energy Fund (FUNAE), which is the apex institution in Mozambique established to tackle the problem of off-grid in rural areas, with more than 24 years' experience, prove the lack of proper energy planning protocols**.** Due to the abovementioned challenges, there is a great need to introduce an energy protocol that will be used as a guideline for mini-grid development in a remote settlement.

The present research is focused on the development of protocols often called standard information models for sizing, planning, and operation of the third-generation mini-grid system, to regulate and promote the good practices of deployment, distribution, and use of energy in remote communities. Therefore, the objective of this study is the **1)** creation of an energy protocol, also known as standard information models, for the third-generation mini-grid system's sizing, planning, and operation, **2)** resize and optimize the mini-grid by considering economic, and technical, and environmental factors by adapting and modifying the features for appropriate energy modelling using different (open-source) tools RAMP to estimate the energy demand and MicroGridsPY model to size and optimize the system. The idea is to propose an energy protocol that can support a sort of standardized procedure for promoting the penetration of a mini-grid.

The application and integration of a similar approach of comprehensive structure may lead towards such aims based on effective and simplest integration of the different stages found in the literature, leading to the framework of Comprehensive Energy Solution Planning (CESP), the so-called energy protocol. The protocol is an assembly of steps and instruments and aims to be the standardized procedure for better sizing and optimization of mini-grids. It consists of several steps that allow us to do Comprehensive energy solution planning and encompasses different activities, see (Fig. 1) representing the flowchart of energy protocol.

The first step of the protocol is a) ***CESP1 - Priority*** consists of the identification of the most important need for the local village, followed by ii) ***CESP2 - Diagnosis and Solution Planning*** phase, where the resource assessment of the existing potential resource and the estimation of the load demand and solution identification of the most suitable technology for power generation is implemented, and sizing the best-optimized system and business and financial model identification is the iii) ***CESP3 – Technical and Comprehensive Design*** phase. The last phase is the iv) ***CESP4 - Impact Evaluation*** devoted to evaluating the activities conducted from the first phase up to the last and analyzing the reliability of the data gathered.

In a nutshell, the achieved outcome of this study will impact positively the scientific area and societal communities. The results of this study will help close the gap between the scientific and grey literature because it is also required for those working in the field, including the private sector, community cooperatives, associations, and government organizations like Energy Fund – FUNAE FP, which was established to address the issue of off-grid energy in rural areas. Additionally, it will offer recommendations to government, utility, and international decision-makers and strengthen international collaboration initiatives that speed up the development and implementation of the smart mini-grid as a substantial and sustainable renewable energy source. The development of energy protocols is crucial for attaining both COP26 and SDG7 goals, particularly in Sub-Saharan Africa (SSA) nations where more than 50% of the population still does not have access to power.

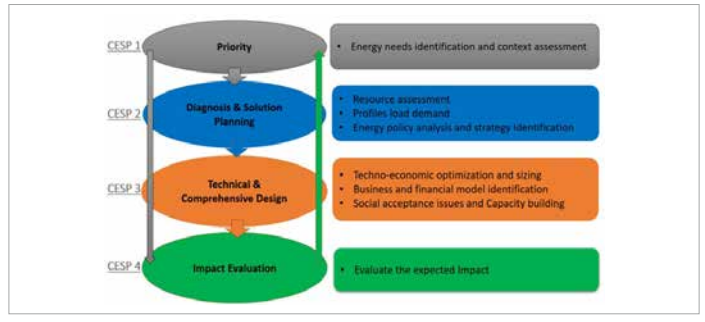

Fig. 1 - Flowchart of Energy Protocol (CESP)

ON THE DEGRADATION OF LITHIUM-ION BATTERIES UNDER AUTOMOTIVE CONDITIONS: EXPERIMENTAL INVESTIGATION, MODELLING ANALYSIS AND EX-SITU VALIDATION

Gabriele Sordi - Supervisor: Dr. Claudio Rabissi

Lithium-ion batteries (LIBs) are the key technology for electrified vehicles. They are expected to spread in the next years. Therefore, an increasing stock of batteries is being put on the road every year and, soon, will become a waste.
Indeed, during operation LIBs performance decreases in terms of power and energy that can be delivered, until they are considered no more suitable for the application. However, the state of health of end-of-life batteries should be estimated, in order to their possible re-utilization in less-demanding "second-life" applications, like small vehicles (forklifts, golf carts), residential energy storage or services to the electric grid. Such estimation should come from extensive studies of degradation mechanisms and determined through a reliable, thorough and fast diagnostic procedures in order to be commercially viable, which are still under development.
Lithium-ion batteries suffer from decay of performance during operation in a rather complex way. Several mechanisms, with strong dependency on the operating conditions (temperature, C-rate, state of charge, number of cycles...) overlap, resulting in a complex performance fade pathway. Understanding and forecasting future performance of a battery is still a challenging task. This work, in the framework of the European Project "DigiPrime" regarding circular economies of different sectors and one industrial project about the estimation of the state of health of batteries from real bus application, dealt with the investigation of lithium-ion battery degradation, as a preliminary activity to evaluate second-life feasibility.
The first task dealt with the development of a methodology and its validation, to provide a physically-sound interpretation of the battery actual performances, potentially scalable to industries. The method combines optimised test sequences with one physical model. The model is applied to reproduce the operation of aged batteries through the update of some parameters value. Due to the large amount of parameters, a preliminary activity dealt with the identification of the most important parameters and their effect on the operation, investigating a large set of operating conditions during three operation types: discharge, electrochemical impedance spectroscopy (EIS) and relaxation after discharge. Two results were derived: a suitable selection of the most meaningful parameters is performed and a reasonable combination of tests and operating conditions is proposed, constituting an optimised protocol that maximizes the identifiability of physical parameters. They allow for a faster and more stable parameter identification procedure, while shortening testing time. The methodology is first applied on a fresh cell and validated against a large dataset of conditions, resulting strongly reliable.
Then, the method is applied on aged cells. One experimental campaign is performed as a case study, involving cycles at sub-ambient temperature. These conditions are known to induce lithium plating as dominant degradation phenomenon.
8 cycles are conducted for 15 equivalent full cycles. The modelling analysis revealed a significant lithium inventory loss and reduction of electrolyte conductivity, consistent with lithium plating, thus confirming the reliability of the method.
As a result, the second task involved a driving cycle campaign, to reproduce the operation of the batteries on a BEV in a laboratory environment.
13 cycles are performed, to reproduce the most common conditions and highlight their role on degradation. Periodically, the campaign is interrupted to perform the optimised protocol, through which the model is parametrised. Meanwhile, two calendar ageing campaigns are also conducted, to investigate the effect of simple storage at 12 combinations of temperature and state of charge.
The analysis underlined how lithium inventory loss is the most important class of degradation mechanisms, among which solid electrolyte interphase (SEI) growth is the most likely phenomenon. Moreover, an important reduction of active material of the positive electrode is recorded, whose magnitude is proportional to the depth of discharge, suggesting a mechanical effect: volume variations, associated with charge-discharge cycles, led to cracking of electrode particles, becoming electrically disconnected. Lastly, worsening of electrolyte and positive electrode diffusive properties explain the reduction of efficiency during high C-rate cycles, associated with a heterogeneous operation. Temperature proved to be a strong driver of degradation, inducing faster lithium loss rate but also degradation of the positive electrode. Cycling is more detrimental than simple storage, but the degradation rate is almost unaffected by the recharge C-rate and the load profile. Differently, state of charge matters both during cycling and calendar operations. Post-mortem analyses are carried out on selected samples to verify the reliability of the results, involving optical and chemical analyses and cyclic capabilities. The estimations of active material loss of the modelling analysis were close to the real value. Moreover, a thick SEI layer was spotted on the negative electrode of the calendar-aged cell, while cracking was evident on cycled positive electrodes.
Lastly, a batch of cells was made available in a private project. These cells were in operation on a hybrid bus for some (from 2 to 8) years. A wide characterization is performed on 40 cells, extracted from different modules of one battery pack, to quantify the residual capabilities. A significant heterogeneity is reported, under both a capacity and impedance point of view. Interestingly, the best performing cells were always positioned in the lower side of the module, where the cooling airstream approaches the module. Differently, cells that are close to the outlet section of the cooling flow were associated with lower residual performances. This information suggested a temperature-driven heterogeneity, supported by the temperature measurements that were collected by the battery management system during the operation on the bus.
The modelling analysis was challenged by a practical problem: the battery type is not commercially available anymore. The following release is exploited as proxy of a fresh cell, even though the differences due to model upgrade are unknown. The analysis identified a significant electrolyte conductivity decrease with loss of lithium inventory, likely to be associated with SEI growth. Ex-situ measurements verified the stability of the lithium-iron phosphate positive electrode, while SEI layer is spotted on the negative electrode surface, as reported in Figure 1.
The methodology proved to be a useful tool to investigate degradation mechanisms, despite there is room for additional improvements.

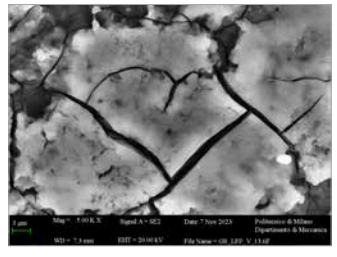

Fig. 1 - Microscopy of the surface of an aged graphitic electrode.

COMPLEMENTING TRADITIONAL COST-BENEFIT ANALYSIS: SDGS-BASED EVALUATION TOOL FOR ENERGY STRATEGY ANALYSIS IN DEVELOPING COUNTRIES

Francesco Tonini - Supervisor: Prof. Emanuela Colombo

The pivotal role of energy in meeting the 17 Sustainable Development Goals (SDGs) of the 2030 Agenda contributes to increasing support for the implementation of energy projects globally, especially in developing countries. It is estimated that the overall amount of investments for energy projects required to achieve all the SDGs before the 2030 deadline is about 4 trillion USD per year worldwide. According to International Energy Agency (IEA) expectations, most of the interventions, 70% in economic value, will be driven by market signals and regulatory policies thus belonging to private sector efforts. Hence, investment decisions need to be well-informed toward a sustainable, reliable and cost-effective energy future. When focusing on private sector interventions, traditional evaluation schemes are based on the bankability of the investments with reference to cost-benefit related indicators, well expressed by Return On Investment (ROI) and pay-back time. However, these indicators are influenced by many debatable assumptions and cannot provide answers to sustainability standards to which the private sector has to refer in response to final consumers' and investors' requirements.

Thus, the need to broaden the investment evaluation perspective complementing traditional financial metrics with multidimensional indicators to capture the complexity of sustainable development. Two different levels of analysis have been investigated in this work:

i) Models and tools able to complement traditional cost-benefit indicators by studying and analyzing future energy projects. It is referred to this as Model-based level.
ii) Benchmarks and evaluation metrics to measure the contribution toward the achievement of various SDGs. Pairwise comparison and decision support system tools were therefore investigated to collect indicators and provide an aggregated measure of the sustainability, in a broad sense, of the projects under study. It is referred to this as Decision Support System level

A novel flexible ex-ante analysis framework is proposed, integrating available models and hybridizing different modeling strategies to adapt to specific cases and analysis requirements, based on SDGs. The framework aims to:

- Measure the performance of private sector energy-related interventions, complementing traditional cost-benefit analysis with a comprehensive SDGs-based framework.
- Capture complex dynamics of the 2030 Agenda by hybridizing available models for integrated impact assessment.
- Provide a modular structure, allowing standalone or integrated application of each module.

The Integrated Impact Evaluation Framework comprises different analysis tools, allowing analysts to obtain a multidimensional dashboard to evaluate project impacts on the 17 SDGs.
This framework enables decision-makers to choose the most sustainable options, complementing traditional cost-benefit analysis. The methodological part of the thesis details novelties introduced for the Model-based and Decision Support System pillars. The Model-based approach involves three components, suitable for standalone or coupled use, while the Decision Support System pillar utilizes the Sustainable Livelihoods Framework for its people-oriented and context-specific viewpoint. Case studies demonstrate the framework's applicability at local and national levels, providing insights into socioeconomic and environmental impacts of energy projects. By integrating Energy System Analysis with Input-Output Analysis, the framework quantifies economic and environmental benefits, shedding light on societal implications and poverty alleviation. The proposed framework's normalization and aggregation procedure, considering worldwide indicators and dividing countries into different tiers, allows for fair comparisons and highlights project impacts on sustainable development dimensions. Overall, the framework offers a structured approach for evaluating energy projects, aiding decision-makers in selecting sustainable options aligned with SDGs and fostering global progress toward a more sustainable future.
A final complete case study is considered aimed at producing applied evidence of the novelties introduced by this work from the theoretical and methodological point of view. Going more into details of the integrated application, the proposed framework is applied to a national-level case study. The target project for this analysis is located in a country in Sub-Saharan Africa where a Natural Gas fuelled combined cycle power plant was deployed which works by consuming the natural gas that previously was flared by their oil production units. This analysis allowed us to extensively analyse future growth scenarios for the nation and understand to which extent the energy project was crucial to sustain the economic growth of the country and which are the beneficial environmental implication of producing electricity from a by-product of the oil industry that previously was flared.
To prove the relevance of applying the proposed Integrated SDGs based Impact Assessment framework, it is worth considering the results of each module step by step and discussing the advantages of integration. The Energy System Analysis allows us to quantify the avoided emissions (Goal 13, indicator 13.2.2), by comparing the new project scenario with the BAU, and the increase in electricity consumption per capita (Goal 7, indicator 7.1.1). As expected, the new project is going to increase the electricity availability for households with zero net emissions from the electricity sector. Analysing the scenario derived from the Energy System Analysis module with the Input-Output module, thus coupling the two, allow us to quantify the relevance that producing net zero emissions electricity has at the economy-wide level. The results show that the project is capable to reduce the overall CO2 intensity of the country. This is the first trade-off that is possible to study with the proposed framework, thus improving the quality of the results at the energy sector level with their implication on the economy. The same Input-Output Analysis module enables to quantify of the socioeconomic effects of the new energy project and related investments, on the country with positive implications for the Economy (Goal 8, indicator 8.1.1), for the society (Goal 3, indicator 3.b.2. and Goal 4, indicator 4.b.1) and in terms of poverty alleviation (Goal 1, indicator 1.1.1). More specifically the Energy Project, considering only backward implications, generates an economic value for the country equal to approximately 11 Million USD per year which represent approximately 1% of national GDP. By taking advantage of the multiplicity of indicators that is possible to derive from the Input-Output analysis it is possible to numerically characterize the relevance of this economic push on the society. The three goals that have been selected show that, even being a huge economic push, it has had approximately null relevance in terms of improvements for basic services such as education and health. Indeed, very limited advantages can be seen by looking at the poverty alleviation indicators. This means that the implementing institution should consider additional complementary actions to promote a stronger impact on society. Results suggest that if the country were able to retain more of the project earnings, it could improve the provision of basic services. These SDGs' indicators results, normalized according to the 5-TIER approach, can be presented in a comprehensive dashboard. These indicators once normalized according to the methodology detailed for the DSS module enable the analyst to provide an overview of the impact in terms of the 5P dimensions and an overall Sustainable Development indicator.

CATALYTIC SYSTEMS FOR ON BOARD APPLICATIONS WITH RENEWABLE FUELS

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Co-Supervisors: Prof. Alessandra Beretta, Prof. Alessio Frassoldati

The original concept of sustainability can be emphasized integrating social goals with responsible resource management and environmental preservation. Today, sustainability is seen as a driver of innovation, which is crucial for competitiveness in a changing world.
Catalysis has historically helped address environmental challenges, such as control of vehicle emissions. The adoption of sustainable renewable biofuels poses new challenges to the development of efficient catalytic technologies for vehicle emission aftertreatment.
This PhD study focuses on two processes: a Rh-based biofuel processor for hydrogen production and a Pd-based system for reducing emissions from a biomethane engine.
We herein briefly summarize the results that were achieved in both research lines.

Ethanol reformer - Bioethanol is a commercial fuel and its on board conversion into a H_2-rich stream can be realized by the CPO (catalytic partial oxidation) process, where the combination of oxidation, cracking and steam reforming reactions can guarantee high conversion and selectivity to syngas in reduced reactor volumes, with contact times of few milliseconds and rapid dynamic response. In this thesis work, a significant step forward has been done with respect to the state of the art towards the development of a complete kinetic model of ethanol CPO that captures all the main kinetic dependences; a combined homogeneous-heterogeneous kinetic scheme has been developed and validated against experimental data in isothermal micro-reactor, informative of the catalytic and thermal activation of the C_2-alcohol.
In fact, starting from a previous experimental investigation in annular microreactor, partial oxidation and steam reforming data were analyzed to derive a comprehensive kinetic scheme of the ethanol activation over Rh. The final kinetic scheme consists of six reactions, whose rate expressions were developed based on the analysis of the effects of the operating parameters (temperature, contact time, feed composition) on the product distribution. One aspect of complexity was represented by the coking tendency of the reacting system, which required the description of C-poisoning phenomena due to the adsorption of C_2-oxygenated species and responsible for a reduction of the rate of ethanol steam reforming. Besides, experiments in the empty reactor revealed that gas-phase reactions can affect the product distribution at temperatures higher than 600 °C and are strongly dependent on the concentration of O_2. In this work, a reduced homogeneous scheme, based on 36 reacting species, was developed starting from a state of the art detailed mechanism, which provided a very flexible modeling tool that can reproduce with accuracy the measured trends with a limited computational load.
The combined homogeneous and heterogenous kinetic schemes have been implemented in a mathematical model of a CPO autothermal reformer, based on Rh/Al_2O_3 coated monoliths. The model, incorporating also all the description of the relevant heat and mass transfer phenomena needed to describe the radial gradients between flowing fluid and catalytic walls, was validated against axially-resolved experimental data collected from the lab-scale autothermal reformer present in the LCCP labs.
It was shown that while the catalytic reactions are responsible for the rapid consumption of the reactants within few millimeters from the monolith entrance, with simultaneous formation of syngas, gas phase reactions are responsible for the formation of C_2 species like acetaldehyde and ethylene that can contribute to surface coking. Consecutive steam reforming of these species, however, limits their formation with a positive effect from water co-feed.

CH_4 emissions - As an additional strategy to support decarbonisation of transport sector, an experimental study was performed to investigate the performances of a commercial Pd based monolith catalyst in the abatement of methane. Different feed conditions – representative of the exhausts of a NG vehicle – were tested by acquiring concentration and temperature profiles through the spatially resolved technique. Experiments were accomplished in lambda sweep operation mode, by testing feeds with both excess and defect of oxygen. Catalyst stability was guaranteed by setting up a protocol consisting in switching periodically to richer compositions for a defined amount of time, this resulting in an almost constant downstream methane conversion.
The application of this novel technique allowed to capture the details of the kinetic phenomena that accompany the decaying O_2 concentration across the monolith channel, whose effects had been so far monitored only on the basis of integral data.
By comparing the catalyst performances at 450 °C for three significative values of lambda (1.02, lean; 0.9963, slightly rich; 0.99, rich), a sharp increase in methane conversion was observed for $\lambda = 0.9963$, corresponding to an increase of methane oxidation rate by one order of magnitude. A correspondent threshold in oxygen partial pressure (PO_2=1.5 mbar) was highlighted as well. When performing the same experiments at 400 °C and 10% water content, the sharp increase in CH_4 consumption rate was detected at richer conditions (λ =0.99). The O_2 partial pressure threshold where the acceleration of CH_4 consumption rate was observed appeared to be shifted towards a lower value (PO_2=0.6 mbar), which was reached only at the richest investigated conditions. This suggests that there is a relationship between the critical oxygen concentration and the reaction temperature, in agreement with literature on PdO/Pd transition.
As it concerns the investigations about water effect, the observed threshold of oxygen partial pressure seemed not to be affected by the variation of water content of the feed.
On the other hand, H_2 and CO oxidation seem not to be affected by the different conditions: they are rapidly oxidized in the first millimeters of the monolith regardless temperature and water concentration, indicating that their consumption rates are under external mass diffusion control.

BUILDING MODELS OF ACCIDENTS AND FAILURES IN ENERGY SYSTEMS BY NATURAL LANGUAGE PROCESSING

Dario Valcamonico - Supervisors: Prof. Piero Baraldi, Prof. Enrico Zio

During the lifetime of energy systems, accidents and failures threaten the system safety, availability and productivity. Learning from past accidents and failures, by identifying the factors that influence their occurrence and severity, constitutes one of the basis of effective decision-making in asset management. Textual reports of accidents and failures, compiled by system operators to describe the events, their causes, their consequences, their severities, and, in case of maintenance, the performed inspection, repair and replacement activities, are typically recorded and stored in repositories. Traditionally, this valuable source of information is not systematically exploited for asset management of energy systems. This is mainly due to: i) the unstructured nature of the textual data, ii) the inhomogeneity of the repositories (e.g. due to the subjectivity of the operators writing the reports), and iii) the large number of reports to consider.

In this context, this PhD work develops a methodological framework for systematically exploiting the information contained in textual reports of accidents and failures in energy systems with the aim of supporting decision-making for asset management. We consider the following two fundamental tasks of asset management: 1) Quantitative Risk Assessment (QRA), which aims at estimating the level of risk and is typically performed during the design phase, and 2) maintenance, which is performed during operation and aims at reducing the number of failures and increasing the availability and productivity of the system.

The developed framework (Fig 1) consists of the three sequential steps of: i) transforming the textual reports into numerical vectors by means of Natural Language Processing (NLP) techniques, ii) identifying the factors influencing accident occurrence and severity by relying on machine learning and expert-based taxonomies, and iii) modelling the events by combining machine learning techniques of classification and clustering with logic and causal models of the accidents and failures. Specifically, NLP models, such as Term Frequency Inverse Document Frequency (TFIDF), topic modelling based on Hierarchical Dirichlet Processes (HDP), Word2Vec and Bidirectional Encoder Representation from Transformers (BERT), have been combined with machine learning techniques, such as Neural Networks (NNs), Random Forest (RF) classifier and Density-Based Spatial Clustering of Applications with Noise (DBSCAN) clustering. Then, Bayesian Networks (BNs) are used for system logic modelling in support to QRA and maintenance.

The effectiveness of the proposed framework is showed considering three real repositories of textual data: a) road accident reports provided by US National Highway Traffic Safety Administration, b) accident reports of process safety events occurring in hydrocarbon production plants provided by an oil and gas company, and c) maintenance reports of freight transport trains provided by a railway company. The PhD work demonstrates the feasibility of systematically exploiting the information content of textual reports of accidents and failures in energy systems. Indeed, the proposed framework allows effectively supporting decision-making at the design phase by QRA and during operation by maintenance analysis.

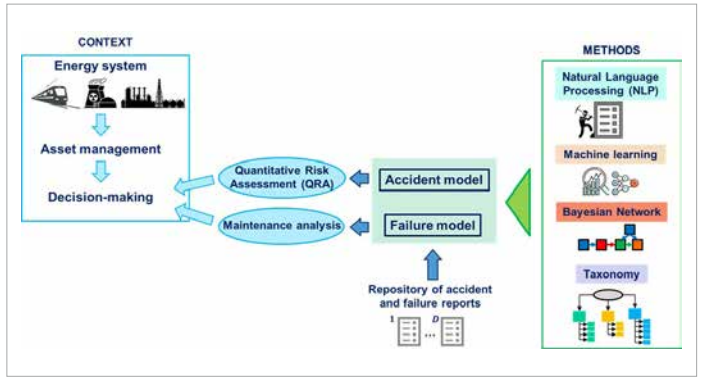

Fig. 1 - Developed methodological framework

PRODUCTION OF NANOSTRUCTURED THIN FILMS FOR NUCLEAR APPLICATIONS USING ADVANCED DEPOSITION TECHNIQUES

Davide Vavassori - Supervisor: Prof. Matteo Passoni
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Thin film science plays a key role in many scientific and industrial areas, including the ones related to nuclear engineering where films and coatings are exploited both for energy and non-energy purposes. Particularly, thin film science is relevant for research applications still at the development stage which can be related to topics significantly different from each other such as laser-driven particle acceleration, the study of nuclear reactions or next-generation nuclear energy systems.
Laser-driven ion sources are an appealing alternative to conventional accelerators. They are based on the interaction between ultra-short (10 - 100 fs) and super-intense (above 10^{18} W/cm^2) laser pulses and target materials. In this respect, Single Layer Targets (SLTs) constituted by foils with a variable thickness between 10s of μm down to several 100s of nm have been widely exploited. Typically, this kind of targets are commercially available and, if composed by a metallic material, they are produced by mechanical rolling. Despite their potential, these sources cannot be considered optimized since a large fraction of the involved pulse energy is not converted into particles energy. The use of advanced target configurations, such as Double Layer Targets (DLTs), represents a promising strategy to increase the conversion efficiency. DLTs are composed by a thin solid foil (e.g., a SLT) on which a low-density material layer is grown by a proper deposition method. The presence of this layer enhances laser absorption, resulting in an increment of the number and energy of accelerated particles. Targetry plays a crucial role also in the study of nuclear reactions. Specifically, in the last years, the ^{11}B(p,α)2α or proton-boron-11 reaction gained interest in different nuclear sectors. This reaction has been studied since the dawn of nuclear physics and the experimental investigation of fundamental quantities, such as the cross section, has been crucial in deepening the understanding of the reaction. Specifically, the detection system and the boron (B) targets adopted in the measurement set-up are resulted decisive in determining the reliability and accuracy of acquired data. Focusing on the latter component, different typologies of natural B or isotopic pure ^{11}B targets have been exploited in the literature, considering both self-supporting foils and films deposited over different kind of substrates.
In this respect, essential target properties for cross section calculation are usually characterized during or after the experiments by indirect methods. Furthermore, thin film science is of interest for the realization of new nuclear energy systems. Specifically, considering both magnetic confinement fusion (MCF) and fission, the presence of liquid metals (LMs) is foreseen in some designs. Regarding MCF, plasma facing components (PFCs) based on LMs are a promising option. In this respect, the use liquid tin (Sn) is studied for some advanced divertor solutions which should allow to avoid or limit several issues (e.g., thermomechanical degradation or neutron damage). Moving to nuclear fission, LM-cooled reactors operating in the fast neutron spectrum have attracted significant attention. Specifically, the lead (Pb)-cooled fast reactor (LFR) offers the possibility to achieve improvements in terms of safety, sustainability, efficiency and costs. In both cases, the contact between LM and structural materials can lead to complex phenomena. Generally, the overall result consists in corrosion or mechanical degradation of the structural material, namely copper (Cu) referring to liquid Sn and steel referring to liquid Pb.
In this regard, the presence of a proper nanostructured protective coating on the surface of interest is a noteworthy solution which has been explored at different extent for the two mentioned applications.
In light of the previous arguments, the production of films with tailored properties emerges as a critical requirement which strictly depends on the deposition technique considered. Among these, Physical Vapour Deposition (PVD) methods are atomistic deposition processes in which films growth occurs because of vapour condensation and nucleation onto a substrate through a vacuum, low pressure gaseous or plasma environment. According to the specific physical process responsible for the formation of the vapour phase, different PVD methods exist. Among these, Pulsed Laser Deposition (PLD) and Magnetron Sputtering (MS) are well-known plasma-based techniques. In the former, the evaporation of material takes place through the ablation of a solid target by laser pulses in a controlled atmosphere. Differently, in the sputtering process, energetic ions generated applying a discharge voltage hit a target material causing the ejection of atoms towards the substrate. Specifically, in the magnetron configuration, the secondary electrons emitted during the process are trapped in the vicinity of the target surface by an externally applied magnetic field. Compared to these more conventional techniques, a step forward can be represented by innovative deposition methods developed in recent years. In this respect, High Power Impulse Magnetron Sputtering (HiPIMS) is worth of consideration. Indeed, the high fraction of ionized sputtered species characterizing this technique allows an improved control on energy and direction of film-forming species, thus offering a new way to deposit film with peculiar properties.
The main aim of this thesis work is the investigation and production of nanostructured thin films and coatings for nuclear areas under development by exploiting different PVD methods. In this framework, understanding the physical mechanisms underlying the deposition process is relevant in view to design films with tailored properties for a certain purpose. Therefore, as initial step, the adoption of a material science approach is worth of consideration to take full advantage of the deposition technique potential. This is especially the case of novel techniques such as HiPIMS which needs further studies to better clarify the relation between plasma characteristics, deposition parameters and film properties. Relying on this activity and according to the requirements of the considered nuclear application, film deposition can be performed with a higher degree of control over material properties which are subsequently characterized and tested.
As previously mentioned, thin films technology already contributed at different extent to the above discussed applications. Nevertheless, further efforts are required.
As far as laser-driven sources are concerned, sub-micrometric SLTs or DLT solid layers are affected by non-negligible local thickness uncertainty due to the manufacturing process. These local variations are relevant in acceleration experiments, resulting detrimental for shot-to-shot stability and reproducibility. Thus, considering the use of the MS technique, the first goal of this work consists in investigating a strategy to produce SLTs and DLTs with improved characteristics. Regarding the ^{11}B(p,α)2α reaction, the knowledge of its cross section still presents some open points. Specifically, the data reported in the literature are affected by the experimental set-up adopted which, in many cases, does not allow the calculation of fully reliable data about cross-section. In this respect, the second goal of the work is the design and realization of B targets through PLD to be exploited for the development of an optimized set-up for cross-section characterization.
Lastly, considering next-generation nuclear power reactors involving the presence of LMs, the interaction between materials and LM is a critical issue to be solved to realize these systems. Therefore, the investigation and characterization of metallic and ceramic coatings potentially of interest to avoid the detrimental action of LM on structural materials is another goal of the thesis work.

TRANSFER LEARNING AND DOMAIN ADAPTATION FOR THE DEPLOYMENT IN PRACTICE OF PROGNOSTICS AND HEALTH MANAGEMENT OF INDUSTRIAL COMPONENTS AND SYSTEMS

Bingsen Wang - Supervisors: Prof. Piero Baraldi, Prof. Enrico Zio

Prognostics and Health Management (PHM) aims at analyzing past, present (recorded) and future (predicted) data and information on the condition of components and systems to detect functional and process anomalies, diagnose degraded and faulty states, and predict the Remaining Useful Life (RUL) of components and systems, i.e., the time left during which the components and the systems will continue to perform their functions.

Two practical challenges are limiting the deployment of data-driven PHM methods in the field: *a*) the data used to develop the model (source domain) are collected from run-to-failure experiments performed in labs, whereas the data which the model is applied to (target domain) are acquired during in-field operation; *b*) the data of the source and target domains are collected from different systems of the same fleet. In both cases, there is a discrepancy between the distributions of the data of the source and target domains, due to the different operating and environmental conditions in which they are collected. Then, traditional data-driven methods, which require that training and test data originate from the same distribution, cannot be successfully applied.

In this context, the objective of the PhD research presented in this thesis is to develop data-driven models for PHM in a way to overcome these practical difficulties. To this aim, methods based on Transfer Learning (TL) and Domain Adaptation (DA) are developed for transferring knowledge and information across different (source and target) data domains, mitigating the effects of domain discrepancies on the accuracy of the models.

Furthermore, in practical applications there are other characteristics of the data, which need to be considered: indeed, data are typically *1*) multi-dimensional raw time series of sensor measurements; *2*) unlabeled, since the ground-truth degradation state is typically unknown; *3*) imbalanced, since failures are rare.

Figure 1 shows the framework of the PHM methods developed by the present PhD work, considering the real data challenges above. To deal with issues *1*), *2*) and *3*) above, in this PhD thesis TL and DA methods are combined with deep learning methods, such as Auto-Encoders (AE), Convolutional Neural Networks (CNN), Long-Short Term Memory (LSTM) neural networks, and adversarial learning techniques.

The proposed methods have been successfully verified considering data collected from various PHM international benchmarks, such as the Aramis Data Challenge, the CWRU and IMS bearing datasets, and the MIT-Stanford battery repository. Finally, the methods have been applied to real industrial data collected from locomotive and railway systems. The obtained results show the superior performance of the proposed methods with respect to state-of-the-art methods.

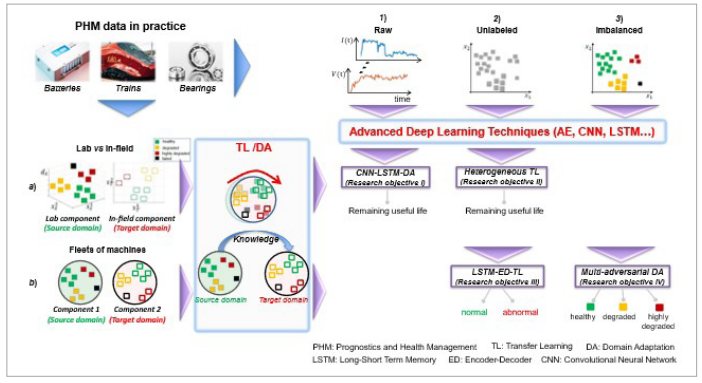

Fig. 1 - Framework of the developed methods.