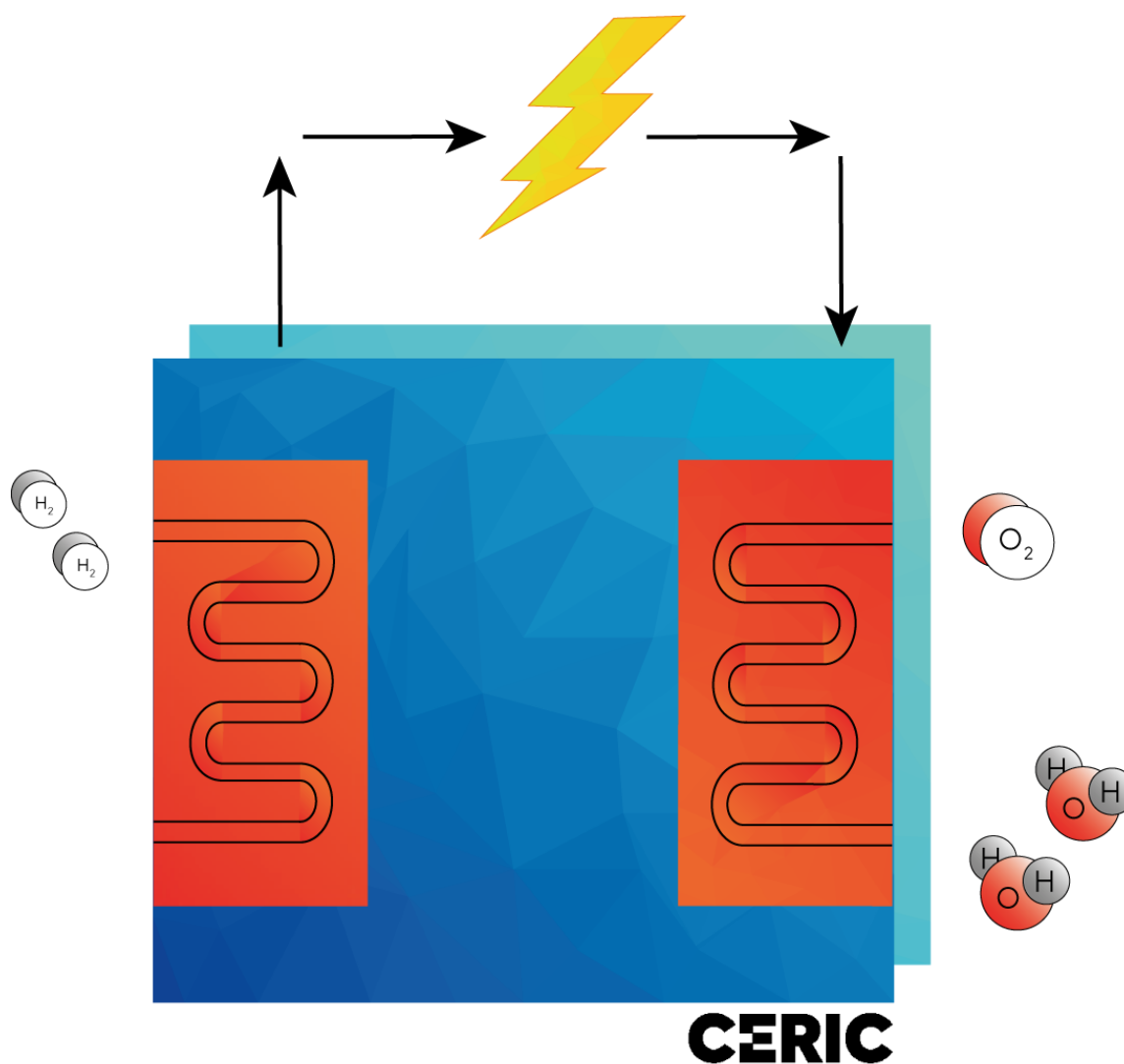


# CERIC-ERIC Expert Group on Fuel Cells

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# 1. Introduction

One of the greatest challenges of our time is to mitigate the global climate change caused by anthropogenic emission of greenhouse gases, mainly generated by use of fossil fuels. A critical part of the solution is to substitute energy generation based on fossil fuels by the more renewable energy sources (solar, wind, geothermal power and others) and one of the main issues is to provide efficient energy storage for a large subset of intermittent energy sources. This can be achieved by various means, such as physical storage (e.g. pump hydro storage, flywheels, compressed air) and/or chemical conversion (e.g. batteries, hydrogen and ammonia generation and storage, artificial carbon-based fuels) (Figure 1). The second family of the energy storage solutions is close to maturity for commercial deployment, therefore research and development proceeds at a fast pace and enjoys significant investments at all levels. For this reason, it is foreseen that the activities in this direction will be an important role for CERIC-ERIC in the near future. While the involvement of CERIC-ERIC in the research on electrochemical batteries has been already discussed in the previous report (Bozzini 2020), the present document on the one hand focuses on the assessment of CERIC-ERIC activities in the field of electrochemical energy conversion by various types of fuel cells and, on the other hand, expounds recommendations to enhance its the role of this fuel cell community.

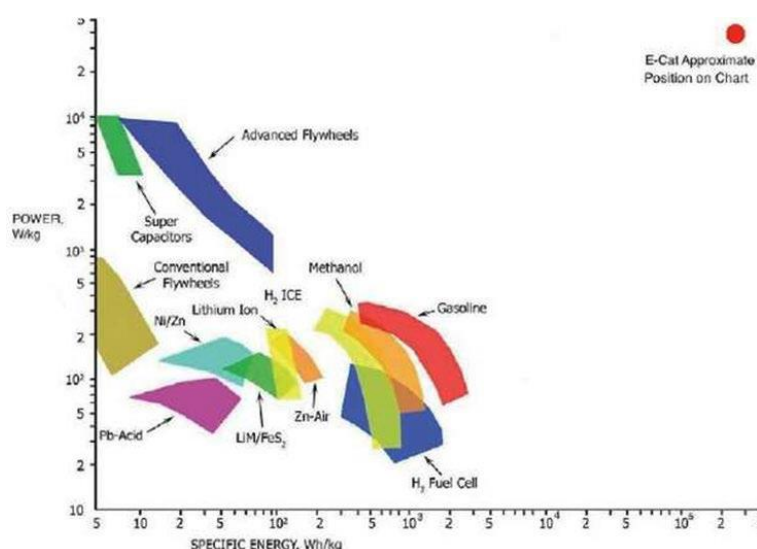


Figure 1: Comparison of different energy storage schemes

A fuel cell is an electrochemical device which converts chemical energy stored in various gaseous or liquid fuels (e.g.  $H_2$ ,  $CH_4$ ,  $MeOH$ ,  $EtOH$ ) directly into electrical energy. This is achieved by harvesting the high energy electrons forming chemical bonds by means of electron transfer into the electrode material. Such direct electrochemical conversion has in principle superior efficiency when compared to heat-based energy conversion, even though implementation into concrete devices and the whole stream from fuel production to utilization in the fuel cell, currently still imply important overall efficiency losses.

A range of fuels can be utilized in fuel cells, but hydrogen plays a prominent role due to its potential abundance, weight and potential carbon neutrality, in the perspective of large-scale green hydrogen production. While lithium-ion batteries are well-positioned for personal transportation and portable applications and other battery technologies – such as flow batteries and some post-lithium chemistries – are appropriate for stationary storage, heavy-duty transportation and large-scale, long-term energy storage are foreseen to be better served by the hydrogen energy storage scheme (Figure 2) (Pellow, Emmott et al. 2015, Cox, Bauer et al. 2020, Nazir, Muthuswamy et al. 2020). In this scheme, sustainably generated (green) hydrogen is not only used to store the energy, but also serves as a chemical precursor

for various key industrial processes. Therefore, the research into the hydrogen fuel cells and hydrogen generation will be an important part of Europe's research activities in the next decade. However, it is important to note that other types of fuel (mainly methane, methanol and ethanol) will still play an important part during the energetic transition, thanks to the high efficiency of associated fuel cells and possible CO<sub>2</sub> sequestration schemes.

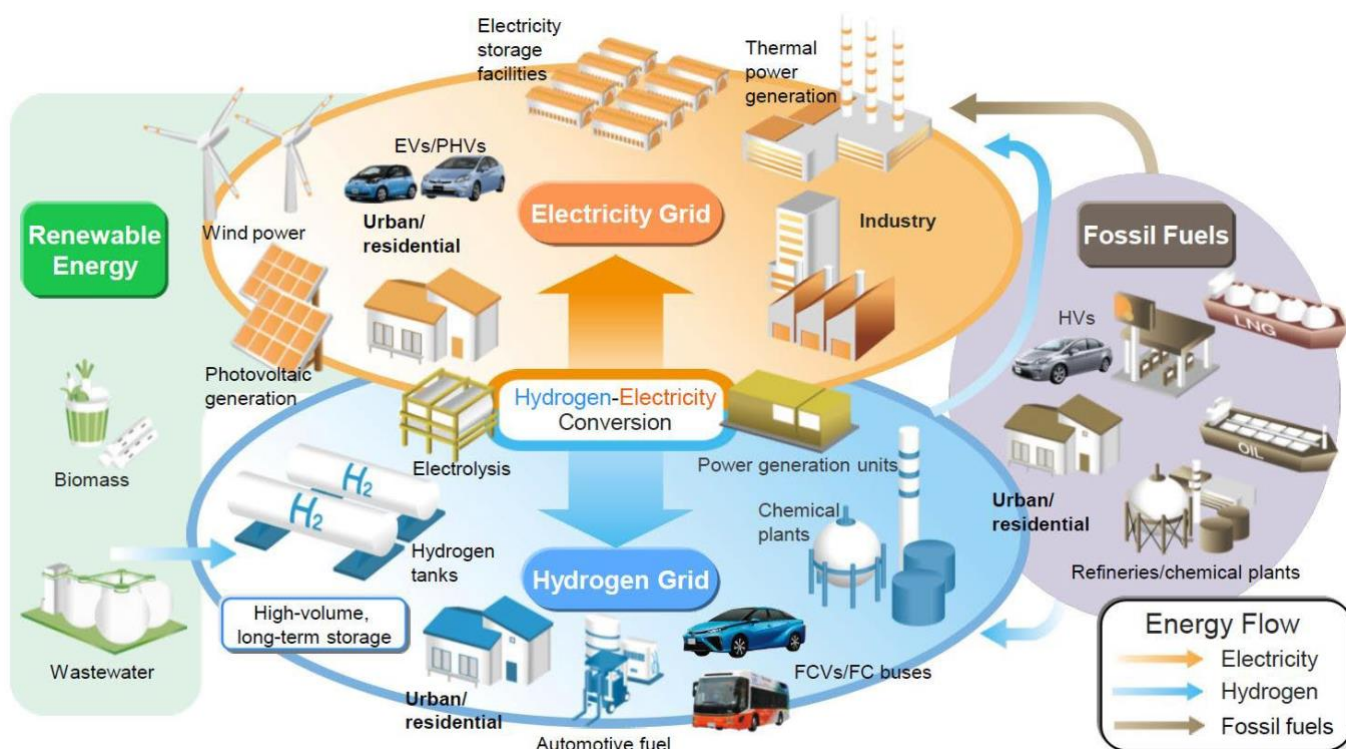
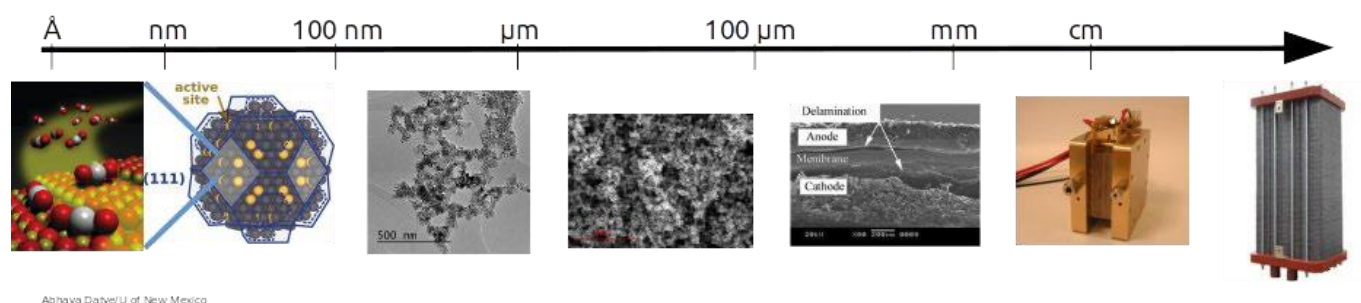


Figure 2: Hydrogen economy schematics

The heart of the mostly used fuel cell device is a membrane electrode assembly (MEA) which, on the one hand facilitates the diffusion of fuel and oxidant to the catalyst layer, and, on the other hand, provides the ion conductive electrolyte (membrane), which electronically separates the electrodes ensuring current continuity. One of the main tasks in fuel cell research and development is to optimize the MEA components for high power density and efficiency, in order for the technology to be economically and ecologically competitive with respect to fossil fuels. With this aim, optimization of material's bulk and interfaces at different length scales is crucial (Figure 3). In this respect the CERIC-ERIC facilities exhibit an exceptionally high potential, as they are well suited for multimodal and multiscale characterisation of materials.



Abhaya Dattya/U of New Mexico

Figure 3: The MEA optimization is a problem which spans 8 orders of magnitude. This makes the multiscale characterisation a necessary tool for further development



Electrocatalyst research, to promote the electrochemical reactions on the electrodes, plays a prominent role in the development of fuel cells. Currently, the most used catalysts are composed of platinum group metals (PGM), often alloyed with a less noble metal, due to their high catalytic activity and stability for reactions involving oxidation of fuels and reduction of O<sub>2</sub>. Search for highly active PGM and non-PGM electrocatalysts with sufficient performance and durability is currently at the forefront of research (Shao, Chang et al. 2016, Banham and Ye 2017, Stamenkovic, Strmcnik et al. 2017), as such materials can significantly lower the cost of the final fuel cell and decrease the need of scarce PGMs. Beside the electrocatalyst research, great effort is put into the optimization of the other constituents of the cell (membranes, gas diffusion layers) which co-define the final performance of the fuel cell device. The main challenge related to proton exchange membranes is their reduction in thickness while avoiding gas crossover and mechanical failure to enhance the device efficiency. For anion exchange membranes, the challenge is even greater, as the OH<sup>-</sup> conductive membranes are less mature (less conducting and less stable), when compared to their protonic counterparts, which represents a major impediment in spreading and commercialization of this type of technology (Vijayakumar and Nam 2019).

From the characterisation perspective, one of the key challenges of fuel cell research is to understand and explain structure-activity-stability trends for device components, which cannot be comprehensively achieved with conventional physico-chemical techniques. Atomistic-level insights, e.g. of the structure of the active sites, provided by CERIC-ERIC facilities is crucial to rationalize electrocatalytic performance and stability. More importantly, understanding the material's behaviour under operating conditions (three-phase boundary, elevated temperatures, acidic environments, etc.) is of extreme relevance. In this context, *operando* measurements can provide unique information regarding the fundamental interactions at the electrode/electrolyte interface as a function of the applied potential and the degradation mechanism of fuel cell key materials.

Therefore, characterisation techniques which provide such information are highly valuable as they can help to understand (i) the complex phenomena leading to degradation and (ii) the interplay between the materials during operation, which is linked to performance losses at the device level. As CERIC-ERIC provides probes with relatively high penetration power, such *in-situ* and *operando* investigations can in principle be implemented, enabling a notable competitive margin for researchers that can have access to them.

## 1.1. Overview on fuel cell technologies

As defined above, a fuel cell is an electrochemical device which converts chemical energy stored in various gas or liquid fuels directly into electrical energy. A fuel cell consists of two electrodes, an anode and a cathode, sandwiched around an electrolyte. Depending on the type of fuel cell, solid (polymer or ceramic) membranes or liquid electrolytes are required and a catalyst layer is deposited on the electrode surfaces. The following paragraphs shortly describe the main types of fuel cell devices and their advantages and bottlenecks.

Whereas in most battery technologies the reactants have to be stored inside the device, in fuel cells they are supplied externally. Some of the advantages of using fuel cells are: emission-free electricity production (in the case of hydrogen-fuelled systems: 2-3 times more efficient than burning fuel), since reactants are supplied externally, the system can operate exclusively in the discharge mode – enabling continuous use –, very high energy density (no reactant storage dependence).

There are many types of fuel cells, each operating slightly differently and thereby having specific applications. A short overview is provided below.

### Alkali or alkaline fuel cell (AFC)

Alkali fuel cells operate with hydrogen and oxygen as reactants and use a solution of potassium hydroxide in water as electrolyte (Ferriday and Middleton 2021). Hydroxyl ions migrate from cathode to anode, where they react with  $H_2$  to produce water and electricity (release of electrons) (Figure 5). At the cathode, electrons react with oxygen and water to produce hydroxyl ions.

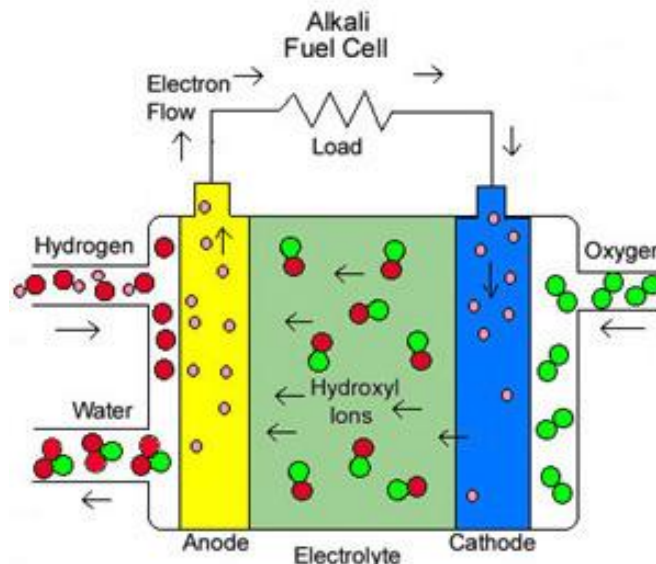


Figure 4: Schematic representation of an AFC.

Alkali fuel cells are very efficient, up to 70%, mostly thanks to the oxygen reaction (very efficient in the alkali medium), with operating temperatures between 150 and 230°C (Arges, Ramani et al. 2010). Operation at lower temperature (<120°C) significantly decreases the efficiency to 35-50%. These so-called Bacon cells, after the initial development of gas diffusion electrodes, were used in space vehicles (Apollo, Space Shuttle aircrafts) as they produce electricity and water.

The typical catalysts for these fuel cells are based on platinum group metals (PGM), which are rare and expensive. However, noble metals are not required for this reaction per se and much research is focused on abundant and metal-free alternatives, which achieve significant activity, but currently still lack stability. There is a major drawback to these fuel cells, though. The alkali cells need very pure  $H_2$ . Even a very small amount of  $CO_2$  present can form solid carbonate. In addition, the KOH medium is very corrosive and there is a significant pressure difference over the cell. New research shows that replacing the liquid electrolyte AFCs with anion exchange membrane fuel cells (AEMFCs) is very promising and the way forward (vide infra, similar to proton exchange membranes). Issues to solve for this technology relate to the electrochemical compatibility among the different electrode components and upscaling (lab to application size AEMFCs).

### Molten Carbonate Fuel Cells (MCFC)

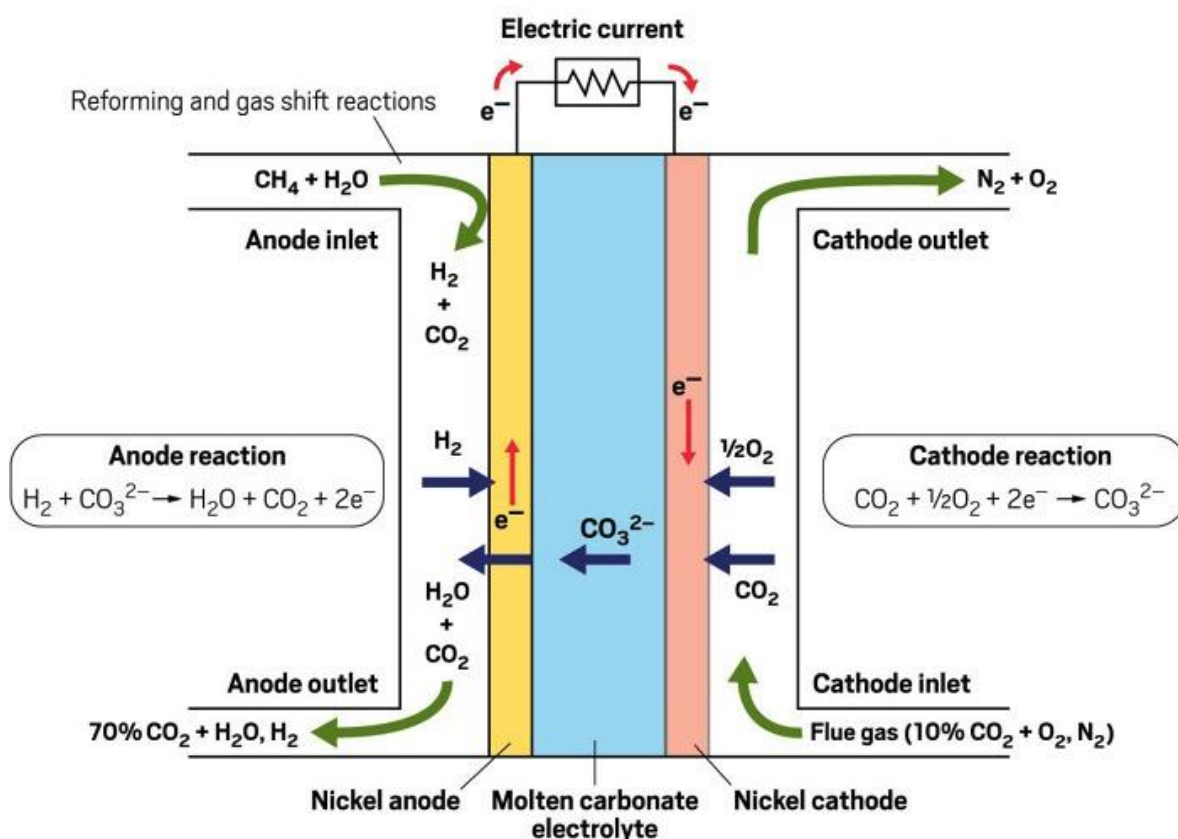


Figure 5: Schematic representation of a molten carbonate fuel cell. Adapted from *Int. J. Hydrogen Energy/IEA*

In a molten carbonate fuel cell (MCFC, Figure 5), operating at high temperatures (650°C), carbonate salts (typically sodium or magnesium) are molten to form the electrolyte, conducting carbonate ions from the cathode to the anode. At the anode, carbonate reacts with  $\text{H}_2$  to produce water, carbon dioxide, and electricity (electrons). At the cathode, oxygen from air reacts with electrons and carbon dioxide (recycled from the anode) forming  $\text{CO}_3^{2-}$  ions. The efficiency of MCFCs ranges from 60 to 80%, with reported output up to several megawatts (MW), with design based on units up to 500 MW (<https://cen.acs.org/energy/FuelCell-Energys-molten-carbonate-fuel/99/i11>).

The high operating temperature combines several advantages and disadvantages: it limits poisoning of the cell by carbon monoxide and allows recycling of waste heat, but limits the choice of materials and compromises safety. Recently, ways have been explored to use the heat produced by high-temperature fuel cell (MCFC, but also solid oxide fuel cells, vide infra) chiefly for the internal reforming of fuels producing hydrogen-rich gas mixtures from natural gas, while generating electricity at the same time (Shikhar, Hemmes et al. 2021).

Catalysts used in these MCFCs are typically based on nickel, which is relatively inexpensive compared to platinum used in other cells. At the same time, the cell does require  $\text{CO}_2$  to be added (in gas inlet), to replenish the carbonate ions from the electrolyte that are used in the reaction. The MCFC is thus an interesting  $\text{CO}_2$  concentrating device, that can ease capture. For several years, people have been looking into the “attachment” of MCFC units to the end of power plants or hydrogen manufacturing plants (e.g. steam methane reforming, autothermal reforming) to pick up the  $\text{CO}_2$  in their exhausts to efficiently capture the  $\text{CO}_2$ , which is diluted and therefore difficult to pick up via other means (see for example (Chiesa, Campanari et al. 2011, Consonni, Mastropasqua et al. 2021)).

#### Proton Exchange Membrane Fuel Cell (PEMFC)



In PEMFCs (Figure 6), the fuel (typically hydrogen) enters the FC and reacts at the anode (catalyst) to form protons and electrons (and heat). The positive hydrogen ions pass through the electrolyte, i.e. a polymer membrane, and diffuse to the cathode. Simultaneously oxygen (O<sub>2</sub>) reacts at the cathode (catalyst) with the electrons and protons to form water (H<sub>2</sub>O).

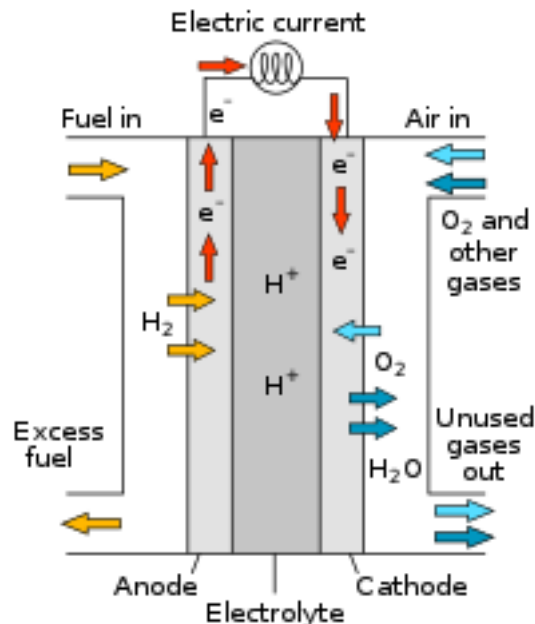
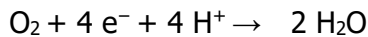


Figure 6: Schematic of a proton exchange membrane fuel cell fed with hydrogen and air.

PEMFCs deliver a high-power density, which is why they can be small and light-weight. The polymer electrolyte (typically PFSA, vide infra) has good ion-conducting properties, allowing these FCs to run at low temperatures (60-80°C) and respond quickly to heat and load changes. The only reaction product is water, and no corrosive liquids are used in the cell, making the FC easy to handle and with limited corrosion risks. PEMFC is a mature technology, commercialised for a variety of fields and applications, such as: telecommunications, data centre and residential markets (primary or backup power), power forklifts and other material-handling vehicles. In particular, its high-power densities and electrical efficiency (40 – 60 %) are well suited to applications where quick start-up is required, such as automobiles: this technology is for instance used for hydrogen fuel cell vehicles (e.g. Toyota Mirai since 2015). The next challenge for PEMFCs is that the advanced performance and lifetime achieved so far could meet the increased efficiency and durability requirements of the heavy-duty vehicle market (truck, bus, locomotive and marine applications) (Cullen 2021). PEMFCs have been developed for pure hydrogen as a fuel, but, in principle, allow the direct use of methanol or ethanol (the Direct Methanol Fuel Cell – DMFC and Direct Ethanol Fuel Cell, DEFC), and can - with the addition of a fuel processor - be used with conventional fuels, like natural gas.

A major disadvantage of PEMFCs is the need for a platinum group metal (PGM) catalyst at both anode and cathode, at fairly high catalyst loading (compared to other FCs). These scarce and expensive metals are the only ones which provide sufficient electrocatalytic activity at the practically used low temperatures and are sufficiently stable. Efforts have been made to optimize the platinum particle size and architecture/nanostructuring and/or mix/alloy the platinum with more abundant and cheaper metals (Ercolano 2018). However, none of these solutions so far have provided stable, active and cost-effective alternatives. Moreover, the presence of even low amounts of CO significantly compromise the catalyst

performance, i.e. CO poisons the catalyst. This means that highly purified hydrogen is required, which substantially increases the costs of the FC. The replacement of PGM by Earth-abundant elements is a crucial challenge, made difficult by the acidic medium of PEMFCs restricting the library of substitution materials. The best candidates reported so far are metal-N-C catalysts synthesized via the pyrolysis of transition metal (Fe, Co), nitrogen and carbon precursors, which achieved ORR activity as high as that of Pt (Jiao 2021). The major challenge remaining is their durability and performance retention over time.

### Anion Exchange Membrane Fuel Cell (AEMFC)

An anion exchange membrane fuel cell (AEMFC) is also known as alkaline anion exchange membrane fuel cells (AAEMFCs), the latter better explaining the operation of the FC (Dekel 2018). The AEMFC is an alkaline fuel cell that uses a (polymer) anion exchange membrane to separate the anode and cathode compartments and is based on the transport of alkaline anions, typically OH<sup>-</sup>. The fuel, hydrogen or methanol, is supplied at the anode and oxygen and water are supplied at cathode. Fuel is oxidized at the anode and oxygen is reduced at the cathode. At the cathode, the oxygen reduction produces the OH<sup>-</sup> ions, that migrate through the electrolyte towards the anode. At anode, hydroxide ions react with the fuel to produce water and electrons. The following reactions take place:

#### *Hydrogen as the fuel*

At Anode:  $\text{H}_2 + 2 \text{OH}^- \rightarrow 2 \text{H}_2\text{O} + 2 \text{e}^-$

At cathode:  $\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^-$

#### *Methanol as the fuel*

At anode:  $\text{CH}_3\text{OH} + 6 \text{OH}^- \rightarrow \text{CO}_2 + 5 \text{H}_2\text{O} + 6 \text{e}^-$

At cathode:  $3/2 \text{O}_2 + 3 \text{H}_2\text{O} + 6 \text{e}^- \rightarrow 6 \text{OH}^-$

AEMFCs have recently received increasing attention, since they allow for the use of non-precious metal catalysts, which significantly reduces the costs. At the same time, significant improvements in the conductivity of anion exchange membranes have led to good cell performance.

### Phosphoric Acid Fuel Cell (PAFC)

PAFCs are fuel cells that use phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) in highly concentrated form (> 95%) as electrolyte (Zhang, Chan et al. 2015). Electrodes are typically made from porous carbon and contain again the expensive platinum catalyst. The fuel cell operates between 170°C and 210°C, with CO<sub>2</sub> containing air as the oxidant and pure hydrogen or a hydrogen-rich gas as its fuel. The efficiency is low, i.e. about 40%. The electro-catalytic reactions taking place are similar to those occurring in a PEMFC. The advantage of this technology is the high temperature of operation, which makes the catalysts less sensitive to impurities in the fuel, and can, for example, withstand CO concentration of 1.5%. The acidic electrolyte is however very corrosive, which puts high demands on the internal parts of the PAFC.

### Solid Oxide Fuel Cell (SOFC)

Solid Oxide fuel cells (SOFC) (Minh 2004) use a ceramic compound of a metal (like calcium or zirconium) oxides as the electrolyte. Because of the use of solid oxides, the operating temperature is very high, i.e. about 1000 °C, with an efficiency of around 60%. Intermediate-temperature versions (ca. 650°C) have also been developed, that enable use of metallic supports, that decrease mechanical issues. At the high temperatures a separate reformer is not required to extract hydrogen from the fuel, and many different

fuels can, in principle, be used, with some issues related to electrocatalyst contamination (Amati 2016). Moreover, precious metals are not required and the FC is less sensitive to impurities in the fuel. The high temperature however complicates cell design and operation, making the cell units fairly costly.

## 1.2. Membranes

The ion exchange membrane lies at the core of the membrane-electrode assembly (MEA). For low-temperature fuel cells and electrolyzers, it is composed of a thin film of ionomer, which is a polymer functionalized either with acidic or basic groups, allowing the transports of protons ( $H^+$ ) or anions ( $HCO_3^-$ ,  $OH^-$ ) (Kerres 2001, Kreuer 2001, Rozière and Jones 2003, Varcoe and Slade 2005, Neburchilov, Martin et al. 2007). The ionomer membrane must be an electronic insulator, forcing electrons to pass through the external circuit of the device. Its main roles are: transporting ions between the electrodes, separating the electrodes to avoid direct reaction of reactant or produced gases and creating a barrier against fluid ( $H_2$  and  $O_2$  gases, methanol...) crossover and providing mechanical integrity to the assembly. This last requirement implies high mechanical strength in both humidified and dry states, low dimensional swelling, high thermal, oxidative and hydrolytic stability, which are properties related to MEA long-term durability. Compatibility with electrodes and low cost are other requirements the membrane must meet.

For fuel cell applications, the conductivity of the ionomer depends on water as an ion carrier, and drastically drops at low relative humidity (RH) and high temperature ( $T > 100\text{ °C}$ ) (Wycisk, Pintauro et al. 2014). To overcome this limitation, the current trend is to minimise membrane thickness ( $\leq 20\text{ }\mu\text{m}$ ) and maximise ion exchange capacity (IEC) (Wycisk, Pintauro et al. 2014). Thin membranes are advantageous in terms of reduced resistivity and enhanced hydration, due to improved water transport during FC operation, while high IEC could ensure ion conductivity at low RH, due to the high charge carrier concentration (Varcoe and Slade 2005, Wycisk, Pintauro et al. 2014). Nevertheless, thin membranes of highly functionalised ionomers present poor dimensional and mechanical properties and high gas crossover, lowering the lifetime of the device (Borup, Meyers et al. 2007, Subianto, Pica et al. 2013). Therefore, membrane mechanical properties are nowadays as critical as ion conductivity and their combination is a crucial challenge for the development of fuel cells and electrolyzers.

Requirements of membranes for electrolyzers are similar to those for fuel cell with two main differences: the membrane is fully humidified (Carmo, Fritz et al. 2013, Vincent, Kruger et al. 2017) and must be able to operate under harsh hydrothermal conditions and to bear high-pressure gradients. Membrane thickness in WE range between 50 and 250  $\mu\text{m}$  (Ito, Maeda et al. 2011, Leng, Chen et al. 2012). As for fuel cells, the main challenge also for electrolyzers is enhancing the device efficiency by reducing membrane thickness and increasing ion exchange capacity (Giancola, Zatoń et al. 2019).

### 1.2.1. Proton exchange membranes (PEMs)

Perfluorosulfonic acids (PFSA) (e.g. Nafion<sup>®</sup>, Aquivion<sup>®</sup>, 3M polymers etc.) are considered the benchmark ionomers for PEM-based electrochemical devices, presenting excellent chemical and thermal stability and high proton conductivity under humidified conditions (Smitha, Sridhar et al. 2005). They consist of a polytetrafluoroethylene (PTFE) main chain bearing perfluorinated side-chains with terminal sulfonic acid groups. The high conductivity of PFSA membranes is correlated with their nanostructured morphology in which ionic nanodomains (mainly responsible for proton transport) are well-percolated and phase-separated from the hydrophobic nanodomains (mainly responsible for mechanical strength) (Kreuer and Portale 2013). The phase-separated nano-structure of PFSA membranes has been investigated by synchrotron-based X-ray scattering and spectroscopy, demonstrating the effect of processing conditions in the chemistry-confinement interplay and in the structure-function relationships. *In-situ* X-ray characterisation allowed to determine the structural changes in PFSA thin films in ambient and humidified environments (Dudenas 2019).

Hydrocarbon-based ionomers have been developed as a cost-effective alternative to PFSA and are used in hydrogen and methanol fuel cells. Among them, we can cite polystyrene sulfonic acid, sulfonated polyimide, sulfonated phosphazenes, sulfonated polybenzimidazoles and sulfonated polysulfone and sulfonated poly(ether ether ketone) (Jones 2012, Siracusano, Baglio et al. 2013, Kraytsberg and Ein-Eli 2014, Zhang, Li et al. 2015). These ionomers present conductivity similar to Nafion® only at very high IEC, which implies high water uptake, resulting in poor mechanical and dimensional stability (Jones 2012). Moreover, some of them suffer from poor oxidative or hydrolytic stability degrading upon operation.

The aim for enhancing MEA performance and lifetime has triggered extensive research on the development of improved PEMs with higher chemical and mechanical strength and fuel barrier properties. This included the preparation of novel ionomers, chemical crosslinking, composite membranes with inorganic fillers and polymer fibre webs (Kreuer, Fuchs et al. 1998, Subianto, Pica et al. 2013, Sood, Cavaliere et al. 2016, Zatoń, Cavaliere et al. 2018, Akrou, Delrue et al. 2020, Waldrop, Wycisk et al. 2020). The investigation of the interface between ionomer and reinforcement e.g. by Raman spectroscopy and Inelastic UltraViolet Scattering would be beneficial to understand the chemical interaction allowing for improved dimensional and mechanical properties (Sood, Giancola et al. 2021).

A strategy to improve the power density and decrease the cost of the PEMFC, is to simplify its design, for instance by increasing the operating temperature. PFSA materials allow to work <100 °C requiring the presence of liquid water for proton conductivity. By increasing the temperature above this value, the catalytic performance of the electrodes will improve, as well as their resistance to poisoning, enabling supply of the PEMFC with less pure fuel without performance loss. This would therefore lead to a gain in power with overall cost reduction. The need for highly conducting and durable membranes working at intermediate temperature (e.g. phosphoric acid doped membranes (Sood, Donnadio et al. 2016)) is also a challenge to tackle with novel materials and doping strategies.

### 1.2.2. Anion exchange membranes (AEMs)

Anion-exchange polymers have a range of polymer backbones and cation groups (Varcoe, Atanassov et al. 2014), (e.g. poly(arylene ethers) (Li, Liu et al. 2013), poly(ether ketones) (Yan, Gu et al. 2014), poly(phenylene oxides) (Rebeck, Li et al. 2013), poly(ether imides) (Wang, Weng et al. 2010) perfluorinated types (Bosnjakovic, Danilczuk et al. 2014), polybenzimidazole (Henkensmeier, Cho et al. 2014). Different types of cation groups were used: sulfonium type (Zhang, Gu et al. 2012), phosphorus-based (Yan, Gu et al. 2014) and coordinated metal-based systems (Wang, Rapakousiou et al. 2014). The N-based cationic-head groups are the most studied for AEM (Varcoe, Atanassov et al. 2014), in particular quaternary ammonium as pendant charged groups (Kreuer 2014), or as part of a heterocyclic/aromatic system (imidazolium (Wang, Wang et al. 2013), benzimidazolium (Lee, Lim et al. 2016), pyridinium type (Miyake, Fukasawa et al. 2014). Varcoe et al. have prepared several anion-exchange membranes with quaternised ammonium groups and polymer backbones using poly(vinylidene fluoride) (Tzanetakis, Varcoe et al. 2005, Varcoe and Slade 2006) and poly(ethylene-co-tetrafluoroethylene) ETFE (Varcoe and Slade 2006) by radiation-grafting (Poynton, Slade et al. 2014) with excellent performance in AEMFC at 60 °C (Gonçalves Biancolli, Herranz et al. 2018). Anion-exchange membranes based on non-fluorinated polymer backbones, for instance high-density (Wang, Peng et al. 2019) and low-density polyethylene (Wang, Brink et al. 2017), have also been described. The latter showed the highest hydroxide conductivity (290 mS cm<sup>-1</sup>) at 110 °C determined so far for an AEM (Douglin, Varcoe et al. 2020). A range of anion-exchange polymers and membranes are commercially available (Fumatech Fumasep® FAA3, Tokuyama A201, Ionomer AEMION™, Dioxide materials Sustainion®, Orion Polymer), with promising properties for electrochemical applications (Henkensmeier, Najibah et al. 2021).

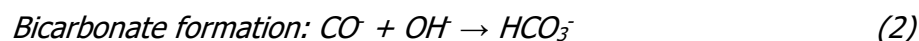
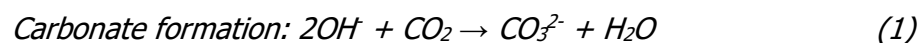
One of the major issues of anion-exchange materials is their limited chemical stability, especially at high pH (Varcoe and Slade 2005). The main mechanism of chemical degradation of the anion-exchange groups has been identified as nucleophilic attack of hydroxide ions (OH<sup>-</sup>) on the polymer backbone (Han, Liu et

al. 2015) or on the pendant positive charged groups (Edson, Macomber et al. 2012). As a consequence, the number of positive charges in the ionomer is reduced over time and the related properties are compromised (e.g. reduction of the ion-exchange capacity and of the ion-conductivity) (Ariyanfar, Ghadamian et al. 2011).

On the basis of the knowledge of these degradation mechanisms, several strategies have been investigated, with the aim of increasing the AEM chemical stability. For instance, large functional groups or electron-donor groups have been introduced on the polymer backbone to prevent the nucleophilic attack by steric hindrance or electronic effects (Hibbs 2013, Ran, Wu et al. 2017). The presence of water plays also a significant role in the chemical stability of the anion-exchange membrane (Dekel, Amar et al. 2017, Diesendruck and Dekel 2018). When the hydroxide ion is solvated, its nucleophilicity towards the quaternary ammonium groups is mitigated due to steric hindrance. Conversely, when OH<sup>-</sup> is incompletely solvated, water molecules only partially shield the hydroxide ions that become more nucleophilic active, leading to membrane degradation (Dekel, Amar et al. 2017). Since the hydration level of the membrane is governed by the operating temperature, the latter is also a crucial parameter.

As for PEMs, enhancing the ion-conductivity by increasing the ion-exchange capacity (Merle, Wessling et al. 2011, Gottesfeld, Dekel et al. 2018) can lead to excessive membrane swelling and mechanical instability (Arges, Ramani et al. 2010). The approaches to reduce this swelling are the same as for proton-exchange membranes: use of reinforcement and ionomer cross-linking (Pan, Chen et al. 2012).

It should be taken into account that ion-conductivity of AEM is reduced as a consequence of contamination by CO<sub>2</sub> present in the ambient air (400 ppm) or dissolved in solution (Ziv, Mustain et al. 2018). The hydroxide anions in the AEM are converted into bicarbonate or carbonate anion according to the following reactions (Siroma, Watanabe et al. 2011):



### 1.2.3. Bipolar membranes (BPMs)

Monopolar membranes are not suitable for devices needing different pH conditions at the anode and cathode sides. These are for instance CO<sub>2</sub>/H<sub>2</sub>O co-electrolyzers or fuel cell and water electrolyzers in which electrocatalysts is active and stable at different pH and eventually PGM-free catalyst can be used. +

To overcome this issue, bipolar membranes can be used, combining both cation and anion exchange properties. Such membranes were initially developed for electrodialysis and are able to maintain a large difference in steady-state pH (up to 14 pH units) while operating efficiently. Bipolar membranes are formed by lamination of an anion-exchange layer with a cation-exchange layer (Frilette 1956). At their interface a hydrophilic bipolar junction (Mafe 1997) is formed. Current work on these materials concerns the optimization of the interfacial layer with 3D architecture (e.g. nanofibers) and water-splitting nanocatalysts for electrolysis applications (Shen, Wycisk et al. 2017, Yan, Zhu et al. 2018). Such interfaces are crucial for the performance of the device and would need specific characterisation techniques at the micro/nanoscale.

## 1.3. Electrocatalysts

The electrocatalyst plays a crucial role in the functioning of all types of fuel cells. It allows the fast electron harvesting needed for the large current densities necessary for practical deployment. The most used catalysts for low-temperature polymer membrane fuel cells are pure or alloyed PGM materials. Lowering the amount of PGM, without compromising the performance of the PEMFC, is essential, as this leads to



significant resource savings, especially for applications in transportation (Whiston, Azevedo et al. 2019). Currently, the most practical and most used catalyst in commercial PEMFC's is still Pt, but it is being slowly replaced by alloy catalysts (e.g. PtNi, PtCo) allowing a moderate decrease in loading inside MEAs (Banham and Ye 2017). Currently, a guiding principle for designing the next generation of catalysts is fine-tuning the active site geometry and altering its chemical properties, through electronic and steric means (Choi, Xie et al. 2013, Chen, Kang et al. 2014, Calle-Vallejo, Loffreda et al. 2015, Li, Zhao et al. 2016, Chattot, Le Bacq et al. 2018).

The high-mass activity is typically achieved by lowering the nanostructure size in that most of the atoms composing the nano-object are located on the surface. While this assures maximum utilization of the material for the electrocatalyst, it also constrains the synthesis approaches and decreases the durability of the catalyst, and therefore research into these two aspects is widespread. The specific activity is, on the other hand, achieved by careful optimization of the reaction sites on the surface of the catalyst. In general, two approaches are common: i) tuning of the surface periodic electronic structure based on DFT predictions (Escudero-Escribano, Jensen et al. 2018, Liu, Zhao et al. 2019) and ii) optimization of surface distortions (Chattot, Bordet et al. 2020, Li, Wang et al. 2020). Both approaches have been successfully used in the development of the next generation of catalysts for PEMFC, such as PtNi octahedra, aerogels, hollow structures and sponges. For this kind of optimization, knowledge of surface (electronic) structure is essential and typically surface sensitive characterisation techniques, such as XPS, Raman spectroscopy and various IR techniques are used.

In recent years, non-PGM catalysts are gaining attention. These are typically carbon materials, often doped with nitrogen or different kinds of metal centres providing active sites through carbon coordination (Dai 2017, Shi, Yang et al. 2020). The main advantage of non-PGM catalysts is their low price, but several disadvantages keep the technology from being massively used. One of them is low specific activity, which, in turn, requires a thicker catalyst layer. Such arrangement is not as performant, due to the limited diffusion of reactants and products. Despite their current shortcomings, these materials promise great potential and are heavily researched. The main characterisation toolbox consists of electron or X-ray based spectroscopies, which are able to accurately determine the coordination of the active sites and their electronic structure.

While the PGM catalysts are also used in AFCs, it is foreseen that for this technology will be competitive with the PEM fuel cells, since the PGM catalyst needs to be replaced by non-PGM materials. On the cathode, this is possible and various non-PGM stable catalysts have been proposed (Bezerra, Zhang et al. 2008, Wu, Santandreu et al. 2016, Miller, Vizza et al. 2017). On the anode side the electrochemical environment is more complex and non-PGM catalysts suffer from high overpotentials, surface passivation by strongly adsorbed OH<sup>-</sup>, low H<sup>+</sup> binding energy and phenyl poisoning from the anion-conducting membranes (Firouzjaie and Mustain 2020). In the high-temperature cells (SOFC, MCFC) the catalyst is typically Ni-, Cu- and Co-based, or composed of various perovskites and other types of solid oxides, and therefore price is not a main constraint in the development of these technologies (Abdalla, Hossain et al. 2018). However, research is still active in this area mainly due to the issues related with the incorporation of the catalyst in the solid electrolyte, its durability in highly corrosive environments and poisoning when used with contaminated feeds.

A specific subject of electrocatalyst research is the investigations of different types of catalyst supports. Optimized supports are essential to tune the triple-phase boundary (TPB) among the catalyst, electrolyte and gas phase. The TPB structure defines the diffusion of the active ionic species to the active site of the catalyst and, to a large extent, it also controls the diffusion flux and supported power density of the catalyst layer. The most common supports are various kinds of carbon-based nanostructures, but recently also metal-oxide supports are being considered (Hornberger, Bergmann et al. 2018, Samad, Loh et al. 2018, Schmies, Hornberger et al. 2018) for their high resistance to corrosion enhancing the electrode (cathode) lifetime. The morphology of the layer plays an important role for the stability of the catalyst particles as well as for the interconnection and electronic conductivity. The metal-oxide supports often

enhance the specific activity through the catalyst-support interactions at the contact boundaries or by modifying the electronic structure of the catalyst nanostructure. For the support effects, electron- and X-ray based spectroscopic techniques, probing the electronic structure of the nano-objects are invaluable (Karuppanan, Panthalingal et al. 2018).

Beside catalyst activity, durability is an important parameter which has to be considered during catalyst development. Often, the catalyst composed from less noble, but cheaper, materials does not withstand the highly corrosive environment in the fuel cell device, especially on the cathode side where oxygen reduction reaction (ORR) takes place. This drawback can, to a large extent, be circumvented by using an alkaline environment, which is compatible with cheaper catalysts, such as Ni or Co. But using these substitutes results in various issues, as discussed above. Given the low stability of other metals at ORR potentials in acidic environments, the only stable catalyst candidate to be used in PEMFC is Pt and its alloys. The stability of such materials can be enhanced by shape engineering and/or surface modification. Even though both approaches have been successfully used, optimizing the catalyst from this perspective remains a challenge (Dionigi, Weber et al. 2019, Fuchs, Drnec et al. 2020, Lopes, Li et al. 2020). The leaching of the less noble metal during the fuel cell operation also causes poisoning of the other parts of the cell and for this reason most of the state-of-the-art catalysts are leached before the deployment. The research into the factors affecting the stability requires physical probes which can penetrate the sample environment and allow *in-situ* and *operando* characterisation. For electron-based probes it is challenging to study surfaces in liquid environments and therefore X-ray spectroscopy and diffraction techniques are better suited as the penetration depth of X-rays is orders of magnitude larger than for the electron probes. Despite this, electron probes undergo a renaissance and new methodologies of *in-situ* and *operando* measurements are being rapidly developed. This is an opportunity for CERIC-ERIC instruments as they could provide such capabilities with certain modifications.

Interestingly, even the most advanced catalysts suitable for low PGM loading MEAs show disappointing beginning-of-life performance in PEMFC devices (Stephens, Rossmeisl et al. 2016, Banham and Ye 2017), even when in laboratory rotating disc electrode (RDE) tests they present activities greatly exceeding the targets. It is believed that the problem is mainly complexity driven (Banham and Ye 2017). The materials in the coated catalyst layer (CCL) (catalyst nanoparticles, carbon support and ionomer binder), and their exact distribution, need to be tailored to a given catalyst. They have to work synergistically to provide free active sites, sufficient flux of reactants to these sites, removal of reaction products and ideal water distribution at high power densities. This is a challenging task and requires careful design not only of the active site turnover frequency, but also its local environment (Ott, Orfanidi et al. 2020). Furthermore, at the MEA level, the reactants and products need to be efficiently transported into and out of the CCL to avoid diffusion barriers that negatively affect the device performance. This is achieved by sandwiching the CCL between proton-exchange ionomer membranes (PEMs) and gas-diffusion layers (GDLs) with carefully designed porosity. Finally, the reactant and product streams are removed from the GDLs mainly through macroscopic flow fields. The diffusion of water across the PEM is also important, in dependence of the operating conditions.

As mentioned above, catalyst, its support and local environment optimization relies heavily on advanced characterisation by electron microscopy and spectroscopy as well as elastic and inelastic X-ray scattering. Given that these characterisation techniques are the main strength of the CERIC-ERIC consortium, the use of CERIC-ERIC instruments in this field is already underway and will likely increase in the future.

## 1.4. Fuel cell durability issues

The practical performance of PEMFCs is controlled by several internal and external aspects, such as: degradation of materials, impurities or contaminants, flow-field design and assembly, operating conditions. Of course, performance degradation is unavoidable, but the degradation rate can be minimized by the understanding of degradation mechanisms and failure modes.

PEMFC performance issues can be classified in terms of: durability, stability and reliability. Durability is the capability to maintain a specified performance level over time: this capability is mainly related to the ageing of materials. Stability is the aptness to recover performance losses during continuous or cyclical operations. Stability decay is typically related to reversible material changes and can be controlled by tuning the operating conditions. Reliability is the potential to perform a specific task for an assigned period of time. The performance decay rate is the combination of both stability and durability decay. In the specific case of automotive applications, the U.S. Department of Energy set the durability target at 5,000 h of operation under real conditions (i.e. dynamic driving cycle with specified changes of current density, gas feed and pressure, relative humidity and temperature) with a maximum performance loss of 10% at nominal power (i.e. 10% voltage loss at maximum current density), corresponding to ca. 0.01 mV/h. In addition to degradation under operating conditions, also off-load transient operations, such as Start-up/Shut-down and cold start, can accelerate degradation.

#### **1.4.1. Catalyst layer degradation**

Among the fuel cell components, the single most critical durability issue concerns the cathode catalyst layer, involving both the electrocatalyst and the carbon support. In the past decade, notable efforts have been devoted to the understanding of the degradation mechanisms of platinum catalyst carbon supported electrode (Pt/C electrode), favored by periodic voltage variations. The performance of these materials depends primarily on the available catalytic active surface and catalyst loading. The catalyst layer degradation is mainly due to platinum dissolution/re-deposition processes, taking place as a result of voltage cycling. Pt-catalyst instabilities are due to a wide range of mechanisms that can be broadly classified according to the scale at which the processes take place. At the micro-scale, Ostwald ripening-based coarsening causes the dissolution of nanometer-sized Pt particles, that diffuse through the ionomer and finally deposit on larger particles (Meier, Galeano et al. 2014). The result is a change in particle size distribution, with a net diameter increase, causing the reduction of available Pt surface (Jahnke, Futter et al. 2020). Voltage cycling favours both nanoparticle agglomeration and dissolution, while temperature and humidity increases the kinetics of Pt dissolution and the mobility of Pt<sup>2+</sup> ions in the electrolyte (Zihlul, Hartung et al. 2016). In turn, the diffusion/migration of Pt<sup>2+</sup> ions plays a key role since diffusion through the polymer electrolyte membrane is followed by H<sub>2</sub>-induced reduction, giving rise to the formation of Pt agglomerates at membrane/catalyst interface, that are disconnected from the current-feeder.

In addition to catalyst particle degradation, also the carbon support tends to undergo corrosion, ultimately releasing loose Pt particles. C oxidation to CO<sub>2</sub> through an adsorbed CO<sub>ads</sub> intermediate is thermodynamically allowed at the operating potential and further favoured by fuel starvation events, yielding CO<sub>2</sub> through an adsorbed CO<sub>ads</sub> intermediate (Li, Zheng et al. 2020). Moreover, Pt-enhanced C-corrosion pathways - resulting from the formation of OH radicals accompanying the reduction of platinum oxides formed at high potentials - have been pinpointed (Maass, Finsterwalder et al. 2008). C corrosion can lead to deep modifications of the triple-phase boundary structure proton and electron transport. In addition, structural collapse of the carbon cathode impairs both oxygen transport product water removal, since void fraction and hydrophobicity are simultaneously reduced.

#### **1.4.2. Impact of operating conditions**

Different stressors concur in promoting Pt and C degradation in the catalyst layer. The factors that promote these processes are similar and thus hard to disentangle. Both are promoted by high temperatures (Li, Moriyama et al. 2015), high relative humidity (Vengatesan, Fowler et al. 2011) and high voltages (Wang, Kumar et al. 2006). Regarding the impact of voltage, potential cycling through oxidation/reduction region emphasizes Pt degradation and dissolution (Harzer, Schwämmlein et al. 2018), cycling at higher potentials, instead, C-corrosion is the key process (Meyer, Pivac et al. 2020).

Start-up and shut-down processes are critical conditions that can lead to catalyst layer degradation. Usually, shut-down in PEMFCs is executed while purging the anode compartment with air. At start-up,

instead, hydrogen is introduced into the anode compartment, displacing air. During both operations, the formation of an air/hydrogen front in the anode generates the so-called “reverse current decay” (Reiser, Bregoli et al. 2005). In these conditions, the portion of the cell filled with fuel operates the normal HOR and ORR. The remaining portion, in which the anode is enriched in oxygen, ORR takes place at the anode and oxidation reactions like COR and OER occur at the cathode. The simultaneous generation and consumption of protons in different positions of the same electrode, causes a reverse proton flow in the air/air and the hydrogen/air regions, leading to a circular current flow in the cell. As a result of this phenomenon, during start-up and shut-down the cell voltage drifts during the transients and the effective local values depend on the location of the boundary between the two regions. In addition to gas-mixing processes, also pseudo-capacitive currents, involving Pt oxides, play a role in degradation phenomena in that they bring about rapid potential changes (Gu, Carter et al. 2019). The space-dependence of these processes leads to the fact that the inlet or outlet sections of the cell are more prone to C-corrosion than the central ones.

Notable efforts have been devoted to the mitigation of the impact of start-up and shut-down processes: addressing both material selection and gas management. As far as materials are concerned, the use of graphitized carbon supports was shown to impart better resist corrosion resistance (Mittermeier, Weiß et al. 2017), while Pt-alloy anode catalysts effectively reduce the ORR activity (Genorio, Subbaraman et al. 2011) and enhance OER activity at cathode (Atanasoski, Atanasoska et al. 2012), thus favouring water oxidation with respect to support corrosion.

Regarding the choice of appropriate operating conditions, control of temperature and humidity and better management of the purge flow are the most common approaches (Jia, Guo et al. 2017). Low temperature and humidity tend to inhibit kinetics and to reduce proton conductivity, selectively reducing transversal migration. High purge flows instead reduce the co-existence time of the oxygen and hydrogen in the anodic compartment. Moreover, circuit-based mitigation strategies have been attempted, such as the application of dummy loads (Yang, Li et al. 2018).

### 1.4.3. Accelerated stress testing

The screening of new materials, cell design solutions and operating protocols demand efficient and reliable benchmarking procedures. Accelerated life tests (AST) are commonly used, that tend to emphasize single degradation processes, that would require thousands of hours of operation under standard conditions to develop. The acceleration rationale is based on the application of higher-than-normal stress level, that concentrates on a single cell component, typically the catalyst layer.

ASTs, though highly useful in principle, currently exhibit three main types of drawbacks, detailed below. (i) Limited generalizability: the results strongly depend on the particular choice of parameters and setup geometries. (ii) Limited representativeness: degradation modes induced by the test are very specific to the selected operating conditions, that generally bear a vague resemblance of real working parameters. (iii) Limited predictive value: it is not easy to translate failure rates assessed in AST to real-world operating lifetime. ASTs so far have been mainly used in a semi-qualitative way, and need to be combined with approaches, such as in *operando* measurements, that would convey a better physico-chemical insight into the nature of stress acceleration strategies.

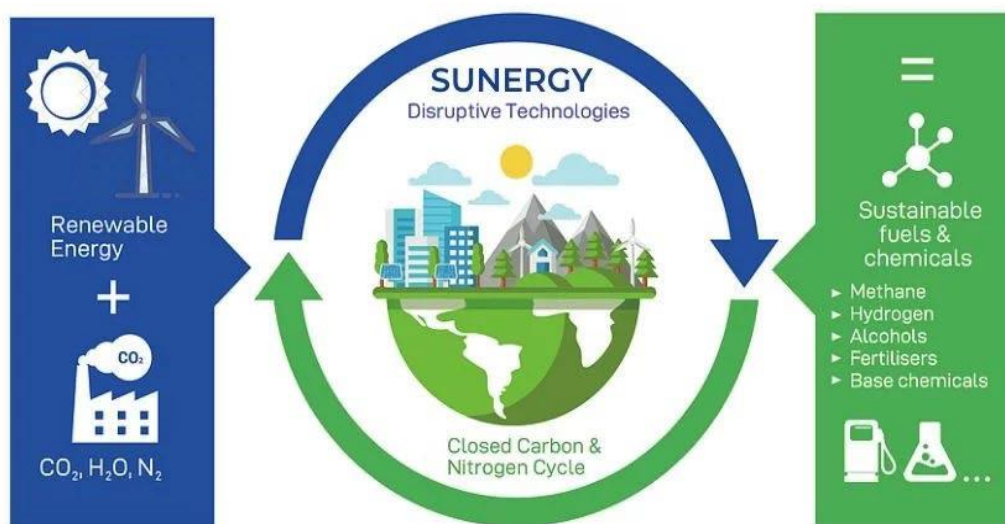
## 1.5. EU initiatives on fuel cells and electrolysis

The EU is strongly investing in the development of fuel cell based technologies and several funding schemes have been activated. Below the main initiatives are briefly presented.

- **SUNERGY** (<https://www.sunergy-initiative.eu/about>), aims at becoming a large European Research and Innovation initiative working towards the conversion and storage of renewable



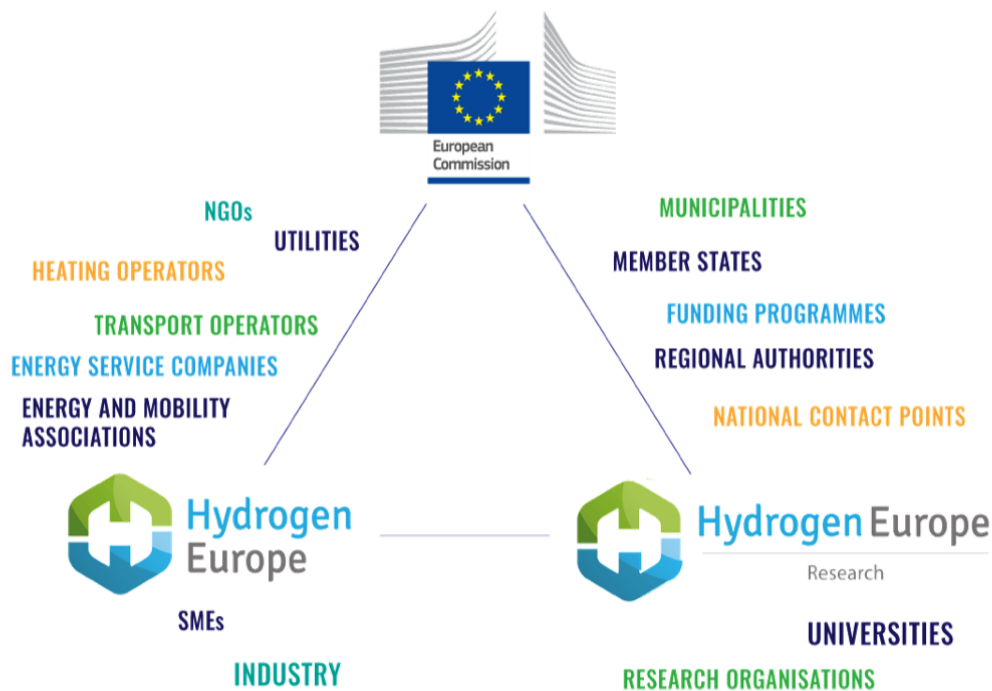
energy into fossil-free fuels and chemicals. SUNERGY unites and builds on two initiatives funded under Horizon 2020: SUNRISE and ENERGY-X. These two projects were selected by the European Commission to prepare for FET Flagship status, a billion-euro programme which identifies "visionary, science-driven, large-scale research initiatives addressing grand scientific and technological challenges". SUNERGY aims to provide solutions to produce fuels and chemicals, and store energy, in a sustainable manner, by using renewable sources (sunlight, wind) and abundant molecules (CO<sub>2</sub>, water, nitrogen), without producing CO<sub>2</sub>. Chosen themes and solutions are: Storage of renewable energy as liquid fuels; Production of fossil-free base chemicals for industry and agriculture; Technologies with a negative CO<sub>2</sub> footprint.



SUNERGY proposes a pipeline of high-impact technologies that can boost efficiency on the supply side by making fuels, base chemicals for industry and agriculture, developing negative CO<sub>2</sub> emission technologies using resources abundant in Europe to enable a circular economy. These actions are part of the Horizon Europe and the Green Deal schemes, contributing to the EU vision of a climate-neutral EU by 2050.

- The Fuel Cells and Hydrogen Joint Undertaking (FCH JU)** (<https://www.fch.europa.eu/>) is a public-private partnership supporting research, technological development and demonstration activities in fuel cell and hydrogen energy technologies in Europe. Its aim is to accelerate the market introduction of these technologies, realizing their potential as an instrument in achieving a carbon-clean energy system. To this aim, FCH JU implements an optimal research and innovation programme to develop a portfolio of clean and efficient solutions that exploit hydrogen as an energy carrier to the point of market readiness. The three members of the FCH JU are the European Commission, fuel cell and hydrogen industries represented by Hydrogen Europe and the research community represented by Hydrogen Europe Research.





In the context of a new Energy Policy, the European Hydrogen & Fuel Cell Technology Platform emphasized the key role of hydrogen and fuel cells in Europe to shift towards new and clean energy technologies. On this basis, the Council Regulation established in 2008 the FCH JU, as a public-private partnership between the European Commission, European industry and research organizations. The Council of the European Union formally agreed in 2014 to continue the FCH JU Technology Initiative and to extend funding under the Horizon 2020 Framework Programme. This phase ran until 2020 and had a total matched budget of at least 1.33 B € provided by the public-private trio. The projects under the FCH JU were aimed at improving performance and reducing the cost of products, as well as demonstrating on a large scale the readiness of the technology to enter the market in the fields of transport. The FCH JU programme is built around three main pillars: transport, energy and cross-cutting. Such activities are designed:

- to accelerate the commercialization of FCH technologies in transport applications through a programme that includes demonstration and research projects;
- to accelerate the commercialization of FCH technologies for stationary fuel cells and for the production of low-carbon hydrogen as an energy source, by increasing efficiency while cutting costs;
- to reduce the costs, producing educational tools and developing analytical methods and test procedures, as well as on the overall impact and dissemination of results.

The Hydrogen Roadmap for Europe

([https://www.fch.europa.eu/sites/default/files/Hydrogen%20Roadmap%20Europe\\_Report.pdf](https://www.fch.europa.eu/sites/default/files/Hydrogen%20Roadmap%20Europe_Report.pdf)) as prepared for the Fuel Cells and Hydrogen 2 Joint Undertaking by 17 members of industries, represented by Hydrogen Europe (*vide infra*). This report described the scenario for hydrogen deployment in the EU based on the perspective of the global Hydrogen Council.

- **Hydrogen Europe** (<https://hydrogeneurope.eu/>) is the European association representing the interest of the hydrogen and fuel cell industry and its stakeholders for a zero-emission society. It

was founded in 2008 by players of the European research community active in the field, with the aim of promoting, supporting and accelerating the deployment of hydrogen and fuel cell technology by aligning the European R&D community and representing it as a whole. With more than 160 companies, 78 research organizations and 25 national associations as members, this association encompasses the entire value chain of the European Hydrogen and fuel cell ecosystem collaborating in the Fuel Cell Hydrogen Joint Undertaking.

The main goals of Hydrogen Europe are:

- promoting best practice, helping companies become more competitive and formulating effective public policy;
- acting as a coordinated voice of industry and research when talking to policy;
- providing the necessary intelligence and a solid network in order to support their members.

## 2. State-of-the-art techniques and facilities in CERIC

### 2.1. Austria

#### 2.1.1. Light scattering experiments (TU-Graz, Austria)

Responsible: Angela Chemelli ([angela.chemelli@tugraz.at](mailto:angela.chemelli@tugraz.at))

##### *Description of the facility*

The dynamic (DLS) and static light scattering (SLS) equipment is hosted at the Institute of Inorganic Chemistry of TU-Graz.

The flat cell SLS instrument consists of a GLG5360 Helium-Neon Laser and an array of 160 photodiodes for simultaneously detecting light scattering curves of suspensions from 1 to 60.

Three different DLS instruments are available:

- DLS - 532 nm: The DLS equipment consists of a laser diode (wavelength = 532 nm, power = 5 W) and a goniometer with single-mode fibre detection optics.
- DLS - 632.8 nm: The DLS equipment consists of a Helium-Neon-Laser (wavelength = 632.8 nm, power = 25 mW) and a goniometer with few-mode fibre detection optics.
- Multispeckle DLS: The Multispeckle DLS consists of a GLG5360 Helium-Neon Laser (wavelength = 632.8 nm, power = 10 mW) and a goniometer with single-mode fibre detection optics.

##### *Current state of fuel cell/electrolysis studies*

So far DLS and SLS studies mainly focused on nanosheet and nanostructured dispersions, with no relation to electrochemical energy conversion. Future research might involve the investigation of ionomer membranes with nanophase separation and bipolar membranes, being intrinsically layered and nanostructured.

##### *Interest of the facility in prospective fuel cell/electrolysis studies*

No specific interest in this field of research was underlined, but the facility may perform studies on new research topics.

#### 2.1.2. Deep X-Ray Lithography beamline (Trieste, Italy)

Responsible: Benedetta Marmioli ([benedetta.marmioli@elettra.eu](mailto:benedetta.marmioli@elettra.eu))

##### *Description of the facility*

Deep X-Ray Lithography (DXRL) is a manufacturing process by which a material, which changes its dissolution rate in a liquid solvent (developer) under high-energy irradiation, is exposed through an X-ray mask to synchrotron radiation. The pattern of the mask is transferred to the material. This is possible by the availability of synchrotron radiation characterised by high resolution, high intensity and extreme parallelism. Microstructures have been obtained with high spatial resolution (200 nm for a wall thickness of 100  $\mu\text{m}$ ), high aspect ratios (up to 40), great structural heights (up to 3 mm) and parallel edges.

Coupled with electrodeposition, casting, hot embossing, moulding, or micro-electroerosion (the so-called LIGA process), it allows using a wide range of materials: plastics, metals and alloys, ceramics. Furthermore, due to the great variety of shapes that can be obtained, it became a very flexible tool for fabricating micro-devices.

DXRL is a key technique to fill the gap between the nano/micro scale (current target of cutting-edge studies) and the macroscale, with the fabrication of microdevices (i.e. microfluidic circuits). This is in high interest for fuel cell applications employing liquids as fuel and/or oxidants. In these membrane-less devices the separation between the cathode and anode liquid streams is achieved by laminarity of the flow.

#### *Current state of fuel cell/electrolysis studies*

There is some past experience with fuel cell technologies at the instrument. The beamline scientist, Benedetta Marmioli, was a consultant for a Cenergy company (Cenergy) providing integrated solutions in the field of energy conversion and storage. Moreover, Benedetta was working on a project for the miniaturisation of fuel cells (using microfabrication techniques). Nevertheless, the fuel cell activity is a recent addition to the instrument and currently there is a research program to develop novel functional materials for fuel cells using controlled irradiation, which is an ongoing collaboration with users. Unfortunately, due to the COVID pandemic, there are still no publications out yet.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

There is a large opportunity, as the potential of DXRL instrument has not yet been fully exploited. It is advised to continue with the current materials research. But other directions should be explored, namely the research into microfabrication of FC devices (in line with the past activity of the beamline scientist) and microfluidic fuel cells. Both of the above technologies have potential of high-impact research and industrial applications. However, the instrument needs systematic collaboration with partners (academic or industrial) to launch research projects and there are no planned activities in these directions, at the moment.

### **2.1.3. Laboratory Small Angle X-ray Scattering (Laboratory-SAXS) facility (TU-Graz, Austria)**

Responsible: Manfred Kriechbaum ([manfred.kriechbaum@tugraz.at](mailto:manfred.kriechbaum@tugraz.at))

#### *Description of the facility*

The Laboratory-SAXS facility consists of a sealed tube X-ray generator (DebyeFlex3000) with three opening ports and shutters where three independent SAXS cameras (A. Paar, Graz, Austria) are attached, one of which can also be used for grazing incidence (GISAXS) studies. Several sample holders for liquid and solid samples are available, with thermostated sample holder stages. Several measurement modes are available:

1. SAXS mode: (1D or 2D detector) with an angular range from 0° to 8° (corresponding to d-values from 100 to 1 nm).
2. SWAXS mode: (SAXS: 1D or 2D, WAXS: 1D) with an additional WAXS range from 17.5° to 35° (corresponding to d-values from 0.5 to 0.25 nm).

3. Continuous SWAXS mode: with an image plate the entire angular range from 0° to 40° is covered.

#### *Current state of fuel cell/electrolysis studies*

The laboratory has no previous experience with fuel cell materials or research in this field.

#### *Interest of the facility in prospective fuel cell/electrolysis studies*

Even though there is lack of experience in the field, the *ex-situ* characterisation capabilities of the instrument are in line with the needs of the fuel cell community. SAXS techniques are routinely used for the morphology characterisation of the catalyst materials and membranes. As the instrument responsible showed an interest in this topic, it is advised that this instrument is added to the core CERIC-ERIC portfolio for the fuel cell research for *ex-situ* SAXS characterisation of catalysts and membranes.

### **2.1.4. Synchrotron Small Angle X-ray Scattering (Synchrotron-SAXS) beamline (Elettra, Trieste)**

Responsible: Heinz Amenitsch ([heinz.amenitsch@elettra.eu](mailto:heinz.amenitsch@elettra.eu))

#### *Description of the facility*

The SAXS beamline at Elettra allows time-resolved studies on fast structural transitions in the sub-millisecond time region in solutions and partly ordered systems with a SAXS-resolution of 1 to 140 nm in real-space, as well as GISAXS measurements to study the structure of thin films and the self-assembly processes on surfaces.

Of the intense radiation of the wiggler photon source, shared and used simultaneously with a Macromolecular Crystallography beamline, the SAXS Beamline uses 3 discrete energies (5.4, 8 and 16 keV, corresponding to 0.077, 0.154 and 0.23 nm, respectively). The beamline optics consists of a flat, asymmetric-cut double crystal monochromator and a double focusing toroidal mirror. An additional wide-angle X-ray scattering (WAXS) detector is also available to monitor simultaneously diffraction patterns. The sample stage is set on an optical table, allowing a versatile optimization of the measurement conditions and the introduction of the users' own specialized sample equipment.

#### *Current state of fuel cell/electrolysis studies*

The beamline recently jointly developed an electrochemical cell suitable for studies of fuel cell catalyst degradation (Bogar, Khalakhan et al. 2020). The interest of the beamline users and scientist in the PEMFC research is highlighted by a recent study of FC bimetallic catalyst degradation (Bogar, Yakovlev et al. 2021).

#### *Interest of the facility in prospective fuel cell/electrolysis studies*

Combination of (GI)SAXS and (GI)WAXS techniques is one of the workhorses in FC research. The combination allows to study the electrocatalysts and other materials consisting the FC in nanoscale. This is a great instrument for *in situ* and *operando* studies in this field and the beamline expertise is an important asset for the CERIC-ERIC services in this field. This instrument should be closely coupled with the electron and X-ray spectroscopy instruments within CERIC-ERIC portfolio, providing joint complementary studies.

## **2.2. Croatia**

### **2.2.1. Laboratory for ion-beam interactions (LIBI) – Section of the Division of Experimental Physics of the Ruđer Bošković Institute (RBI) (Zagreb, Croatia)**

Responsible: Dr. Milko Jakšić ([milko.jaksic@irb.hr](mailto:milko.jaksic@irb.hr))

### *Description of the facility*

The LIBI facilities are centred around two electrostatic tandem accelerators (6 MV EN Tandem Van de Graaff and 1 MV HVE Tandetron) both feeding 9 beamlines, 5 out of which are accessible through CERIC. A system of quadrupole lenses (doublet, triplet and quintuplet) focuses the ion beam to a micrometric spot: details on spot size depend on the type of ion, energy and current, but can be as low as 0.25 mm. The available beams are: protons (0.4 to 8 MeV), most of other heavier ions (up to ME/q<sup>2</sup> ratio of 15 MeV). The typical current range is 1,1000 pA, with fA capability for low-current methods, such as STIM and IBIC. The Van de Graaff accelerator features a multicathode sputtering ion source for all ions, except He ones, that can be generated with a RF gas source with Rb charge exchange. Heavy ion beams produced by the Van de Graaff are generally used for ERDA (e.g. Au, Cl, I), fusion-related experiments (e.g. Cu, Fe, W) and detector investigations (e.g. C, O, Si); light ions (3He, 4He, Li) are typically employed in analytical methods (RBS and NRA) and protons are applied chiefly for charge-transport studies. The Tandetron accelerator employs a duoplasmatron ion source with Na charge exchange, for 3He and 4He beams and a sputtering source optimized for H, Li, C, O, Si, Cl and Cu ions.

The ion beam and nuclear microanalysis activities based at LIBI are focused on three key areas: (i) analysis of elements and isotopes with MeV ion beams (current range: pA, nA); (ii) characterisation (e.g. crystal structure, morphology, density, charge transport) with MeV single ions (current range: fA) and (iii) material modification by ion irradiation.

*Analytical methods* address elements (PIXE, RBS, ERDA) and isotopes (PIGE, NRA). PIXE relies on the detection of ion-beam induced X-rays, while RBS and ERDA are carried out by analyzing backscattered and recoiling ions. Isotope-analysis methods depend on the measurement of gamma rays (PIGE) and particles (NRA) generated in ion-beam induced nuclear reactions.

PIXE exhibits ppm sensitivity and can address elements with atomic numbers in the range 11,92. RBS is more sensitive to light elements and is thus complementary to PIXE, as far as elemental analysis is concerned, but it is also employed for elemental depth profiling with near-surface sensitivity. In a way similar to RBS, but detecting forward-scattered ions, ERDA exploits elastic nuclear interaction between the ions of the beam and the atoms of the sample to perform quantitative elemental analysis for a wide range of elements (from hydrogen to rare-earth elements) with ca. 0.1% sensitivity and depth-profiling capabilities. Elemental analysis, especially of low-Z elements (such as: Li, Be, B, C, N, O, F, Na, Mg and Al), can be performed also by detecting particles or gamma rays generated by nuclear reactions caused by ions can penetrating into the nucleus. Measurement of particles and gamma rays are employed for NRA and PIGE analyses, respectively.

*Characterisation techniques* exploit: (a) the transmission of ions (STIM) for density measurements; (b) the induction of charge pulses (IBIC) for charge-transport quantification; (c) ion channelling for crystal structure determination and (d) secondary electron emission (SEI) for morphology estimation.

STIM is carried out by measuring the energy of appropriately selected transmitted ions, that bears information variations in structure and density of the sample. IBIC relies on charge-pair formation as a result of ion beam interaction with the sample, conveying information on charge-collection and electric transport properties of a semiconductor, with depth resolution, enable by injection of different ion species with different energies.

Material modification by ion-irradiation can be performed at two beamlines that can be accessed through CERIC: DiFu (Dual ion-beam end station for fusion materials research) and Dual Microprobe, with microbeam focusing capabilities, that is currently still under construction. These instruments were designed for flexible irradiation, using a wide range of ion-beams and energies. At the moment of this writing, this approach seems to out of the scope FC studies.

Below, we are reporting concise details on the beamlines affiliated to CERIC and on the methods implemented therein.



Beamline #1: RBS/PIXE: Particle-Induced X-ray Emission and Rutherford Backscattering

This beamline is generally fed with a proton beam (typically 2 MeV, 1, 10 pA) with a circular spot size that can be adjusted in the range 3, 8 mm. Samples are loaded automatically with a charger that can host 16 items. The instrument is equipped with two semiconductor detectors for PIXE, dedicated to lighter and heavier elements, respectively and an RBS detector.

Beamline #2: Nuclear Microprobe

This instrument is dedicated to ion-beam experiments, of all sorts detailed above, with high lateral space resolution (down to 250 nm beam spot size), achieved by scanning the ion-beam over the sample surface with a field of view of 1 ´ 1 mm<sup>2</sup>, with a flexible choice of ions and energies. Typical currents employed for PIXE, RBS, NRA and iono-luminescence lie in the range 1, 1000 pA, while fA beams can be produced for STIM and IBIC.

Beamline #3: ToF-ERDA: Time-of-Flight Elastic Recoil Detection Analysis

The ToF-ERDA instrument employs beams of both protons and heavy ion (such as Cl, I, Au) with energies of up to 40 MeV, to recoil atomic nuclei from the sample in the forward direction. Measurement of energy and time of flight of the recoiled nuclei, enable separation of all elements by energy and mass in the same experiment, allowing depth profiling, based on energy distribution of heavy recoiled ions, with depth resolution down to 5 nm for C, N and O. Since forward recoil requires grazing incidence, only samples with low roughness (≤10 nm) can be studied. Energy analysis mandates UVH in the analysis chamber. The system is equipped by two detectors: for energy, a gas ionization detector is used, while the time-of-flight detector consists in two space-separated timing gates, using LiF-coated foils for the detection of the passing ions by electron emission resulting from ion-foil interaction.

Current state of fuel cell/electrolysis studies

The chief ongoing research activities of LIBI are in the fields of: (i) development of methods (SIMS with MeV ions, application of RBS for Si-based electronic devices, high-resolution X-ray spectroscopy, ion-beam induced luminescence) and detectors (diamond-based radiation detectors); (ii) materials science (photovoltaics, materials for nuclear fusion reactors); (iii) biological and medical sciences (SIMS of organic materials), environment studies and archaeometry.

Ion beam analysis methods are suitable for the characterisation of hydrogen as well as other elements employed in FC materials. Specifically, PIXE can be used for the 2D mapping of dissolved and reprecipitated metallic components of electrocatalyst metals in the ionomeric membrane of PEMFCs. Furthermore, elastic recoil detection analysis (ERDA, RBS and STIM) can be used to determine the depth and density distributions of FC components, enabling 3D imaging with lateral resolution down to 1 ´ 1 µm<sup>2</sup>. In the case of hydrogen, the detection efficiency is normally low, but IBIL has performed some instrumental improvements (especially in the ToF-ERDA beamline) in order to increase detection efficiency and to make their spectrometer more suitable for hydrogen analysis, achieving a sensitivity of tens of ppm with a surface depth resolution of ~15 nm: in the microprobe mode, 3D analysis of hydrogen is can thus be achieved.

Specific ion-beam measurements, documented in the literature for FC studies are summarized below.

- (i) *Hydrogen and alcohol Polymer Electrolyte Membrane FCs (PEMFC).* The accurate determination of Pt loading (Abaoud 2003, Tamai 2003, Abaoud 2005) as well as the analysis of Pt dissolution/precipitation in PEMFC MEA were carried out by PIXE (Williams 2009, Gunther 2012). RBS was used to measure the total content of Pt (Brault 2004) deposited by plasma sputtering and to quantify Pt penetration into the porous diffusion layer of PEMFC electrodes as well as the Pt loading and in-depth distribution MEAs (Cavarroc 2009). The composition of Zr-O-N based ORR catalysts for PEMFCs as a function of preparation conditions was investigated by RBS and accurate N and O analysis was based on NRA (Doi 2007). Moreover, RBS allowed to measure Pd and Pt profiles in GDLs bearing PtPd electrocatalysts (Mougenot 2011, Caillard 2015) and to determine the amount of Pd, Ni and Sn in carbon-supported

electrocatalysts for DEFCs (Moraes 2016) as well as the distribution of Ru in the catalyst layer of a DMFC (Wang 2006).

- (ii) *Solid Oxide FCs (SOFC)*. Proton conductivity in a ceramic proton-conducting electrolyte for Protonic Ceramic Fuel Cells was studied with ERD and NRA, by measurement of the local hydrogen concentrations at the micron scale (Berger 2012). Moreover, ion-beam methods found application in the study of oxidation-resistant coatings of metal plates for SOFC bipolar interconnects: composition of the coated plates and the rate of oxidation were measured by RBS and NRA (Garratt 2009), ToF-ERDA (Putkonen 2002), RBS and PIXE (Chen 2008) and RBS and NRA (Smith 2004).
- (iii) *Molten Carbonate FCs (MCFC)*. Lithium concentration and in-depth distribution in NiO cathodes of MCFC were determined by PIGE (Belhomme 2000) and PIGE/PIXE (Boni 1990).

#### *Interest of the facility in prospective fuel cell/electrolysis studies*

LIBI declares interest in FC studies, but at the moment neither expertise nor dedicated manpower is available. Preliminary liaising with experts in the field who can help focus possible activities and a small amount of funding to hire a student with this focus would boost the start off on FC studies with LIBI Instruments.

The sample environments available at the beamlines can host FC material samples and possibly model systems for *in-situ* work can be reasonably easily adapted to the sample stages. Dedicated preliminary assessment in collaboration with external experts would foster prospective access of users from the FC community.

## 2.3. Czech Republic

New large research infrastructure (LRI) projects funded by the Czech Ministry of Education will start in 2023. An extension of the actual LRI Surface Physics Laboratory – Materials Science Beamline to a new LRI will be proposed: Surface Physics Laboratory – Hydrogen Technology Center. The center should enable open access to FC and WE test benches with dismountable research single cells and short stacks, catalyst printing line, *operando* fuel cells and electrochemical cells, RDE, electrochemical AFM, Enviro ESCA, NAPXPS, MEA preparation laboratory involving customized sub-gasket cutting and hot pressing. Users would also have access to PEMFC testers up to 50 kW in the CU-Industrial partner Joint testing laboratory equipped with a 200 kg of hydrogen storage facility, under construction by industrial partners. Further current plans with respect to Fuel Cell research are:

- In 2021 EnviroESCA will be open for user access
- In 2021 a prototype of a 3 kW open cathode stacks with 7-MEA based on homemade CCMs and metallic/polymeric graphite BPs will be tested.

### 2.3.1. High Resolution Field Emission Scanning Electron Microscope (FESEM) (Charles University, Prague, Czech Republic)

Responsible: Iva Matolínová ([imatol@mbox.troja.mff.cuni.cz](mailto:imatol@mbox.troja.mff.cuni.cz)) and Vladimír Matolín ([matolin@mbox.troja.mff.cuni.cz](mailto:matolin@mbox.troja.mff.cuni.cz)).

#### *Description of the facility*

The FESEM laboratory is located in the Department of Surface and Plasma Science at Charles University. The FESEM uses a high brightness Schottky emitter as the electron source allowing to tune the acceleration voltage from 200 V to 30 kV, or 100 V to 30 kV with beam deceleration (BD). Compared to a conventional

SEM, it produces clearer, less electrostatically distorted images, with spatial resolution down to 1 nm. The Tescan Mira3 instrument is designed for high vacuum (HV) operation and is also rigged with detectors allowing electron back-scattering spectroscopy (EBS) and energy dispersion X-ray spectroscopy (EDX) for chemical element mapping of surfaces with sub-micron resolution.

Beside open access machines, other supporting experimental setups are available: FIB-SEM (catalyst lamella preparation for HRTEM), electrochemical AFM, fuel cell testing laboratory with 10 test benches, 2 RDE with bi-potentiostats, two magnetron sputtering systems for catalyst deposition, laser cutter, SONO-TEK ultrasonic spray deposition system for CCM and CCGDL preparation.

In the frame of a technology transfer they are expecting to mold first polymeric graphite 100 cm<sup>2</sup> bipolar plates at the end of the year. They are developing Rotogravure catalyst printing system for CCM production and working on metallic 100 cm<sup>2</sup> bipolar plate development (metallic cathode BPs are actually tested in an open cathode short stack).

#### *Current state of fuel cell/electrolysis studies*

SEM, in combination with EDX and FIB techniques, is widely used for the characterisation of various materials, among which catalysts and membranes for hydrogen fuel cells and water electrolyzers (Kůš, Ostroverkh et al. 2019, Yakovlev, Nováková et al. 2019, Hrbek, Kůš et al. 2020, Khalakhan, Supik et al. 2020, Nováková, Dubau et al. 2020).

### **2.3.2. Near Ambient Pressure X-ray Photoelectron Spectroscopy (Prague, Czech Republic)**

#### *Description of the facility*

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique, which measures the elemental composition, empirical formula, chemical state, and electronic state of the top approximately 10 nm of a material. Running the X-ray source and the electron analyzer requires high vacuum ( $P \approx 10^{-8}$  mbar) conditions in the analysis chamber and, therefore, conventional XPS is possible only under UHV conditions. Near-ambient-pressure XPS (NAP-XPS) is an XPS system capable of operating at pressures of a few tens of millibars, allowing to study chemical interactions on the atomic level for vapour–solid interfaces. NAP-XPS also allows one to investigate electronic and structural properties of small organics., making it difficult to conduct investigations of surfaces under real-world conditions (i.e. in the presence of gases and possibly liquids). The NAP-XPS facility works in strong cooperation with the Material Science beamline at Elettra synchrotron (Trieste, Italy).

Various electrochemical setups, which can be used for fuel cell research, are available for CERIC-ERIC users:

- 1) An electrochemical cell equipped with Pt wire as counter electrode and AgCl as reference. The main purpose of the cell is to avoid air exposure during electrochemical measurements and XPS measurements on post-mortem electrodes. The electrode and the electrolyte are in contact only upon voltage bias, then the electrode is removed, dried, evacuated and transferred to analysis chamber. An additional buffer chamber serves as the transition chamber for sample transfer between the electrochemical cell and the (UHV) transfer chamber through an inert atmosphere (Ar).
- 2) An *in-situ* electrochemical cell has been developed by the Erlangen-Nurnberg University and used in the NAP-XPS station, allowing to study the electrode-electrolyte interface under working conditions. However, it is not available to the user community.
- 3) Currently the instrument team develops a new design of NAP cell which will allow characterisation of materials in MEA's.
- 4) A SP50 Biologic potentiostat is available for users.

*Current state of fuel cell/electrolysis studies*

In general, there is an experience with fuel cell research at the instrument. The instrument scientists have been involved in the past in a fuel cell lab doing preparation of fuel cell catalysts and its testing in RDE and PEMFC. Further, Bretislav obtained a JSPS fellowship at the National Institute for Materials Science in Tsukuba, Japan ('Design of interface and surface on platinum less electrocatalysts for polymer type fuel cells').

The instrument is used by various high profile groups who focus their studies on model (electro)catalyst surfaces and materials for SOFC (Prof. Libuda and Prof. Bozzini). These collaborations resulted in several high impact publications (Faisal, Stumm et al. 2018, Bozzini, Previdi et al. 2019, Brummel, Lykhach et al. 2019).

*Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

This facility is already well established in the field of materials research for fuel cell technologies. The ability to determine the electronic structure at near ambient conditions is an important CERIC-ERIC asset in the fuel cell research. That is because the catalytic activity of materials is typically governed by its electronic structure and therefore electronic structure is one of the most common targets in electrocatalyst optimization. It is well known that the electronic structure is affected by the actual environment in fuel cell environment and determination of the electronic structure in working conditions is uttermost importance.

According to the instrument scientist, there is also a large interest to continue in this direction and various advancements are being planned (new NAP PEMFC device). However close collaboration with CERIC-ERIC facility specialized for structural characterisation (SAXS, XRD) is being advised in order to provide CERIC-ERIC users complete workflow for *in-situ* characterisation tailored for electrocatalyst materials. This will increase the value of CERIC-ERIC facilities as for full understanding of the material functioning, both electronic and structural information is needed and such characterisation workflow is often requested.

**2.3.3. X-ray Photoelectron Diffraction (Prague, Czech Republic)**

Responsibles: Kateřina Veltruská ([veltrusk@mbox.troja.mff.cuni.cz](mailto:veltrusk@mbox.troja.mff.cuni.cz))

*Description of the facility*

XPD is a crystallographic technique combining information on morphology, electronic structure and chemical composition of the material. This technique provides a direct structure determination tool and is best suited for applications on periodic surfaces, such as oriented single-crystal surfaces, ordered adsorbate layers on crystalline substrates, or thin epitaxial films. Due to its high sensitivity to the surface structural details on the local scale, an XPD analysis can also be performed on systems lacking long-range periodicity, e.g., small atomic surface complexes and supported nanoclusters.

The suitable samples must be electrically conducting, ultra-high vacuum compatible (stable, low vapour pressure), and with negligible roughness. For this purpose, an *in-situ* sample preparation is mandatory: electron beam stimulated evaporation sources are in place in the experimental chamber and reactive sputtering is available in the preparation one; then, Argon ion surface cleaning and sample heating in the UHV, up to approximately 1000 °C, can be used to prepare the surface of the sample.

Two kinds of radiation sources are available to produce X-rays (Mg or Al K $\alpha$ ) or UV (He I,II lamp) photons, corresponding to higher and smaller penetration-depth, respectively.

*Current state of fuel cell/electrolysis studies*

The instrument provides service for local and CERIC users. No particular research in FC field is foreseen and there are no CERIC users in the field of FC research using this instrument. The instrument published several publications studying electrocatalysts as part of local collaborations.

### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

There is a plan to build an electrochemical cell coupled to the instrument which would open the possibilities for quasi *in-situ* experiments. This can be an interesting addition to the CERIC portfolio. In the meantime, this instrument can be used for *ex-situ* characterisation of FC materials.

## 2.4. Hungary

### 2.4.1. Budapest Neutron Center (BNC) (Budapest, Hungary)

Responsible: Dr. Tamás Belgya ([tamas.belgya@energia.mta.hu](mailto:tamas.belgya@energia.mta.hu))

#### *Description of the facility*

BNC is built around a 10 MW BWR (light-water cooled and moderated, with a Be reflector) tank-type reactor, fueled with 20% enriched uranium, yielding a thermal flux of the order to  $10^4 \text{ n cm}^{-2}$ . The research experience of BNC is principally focused on: neutron diffraction and scattering, elemental analyses and imaging. The methods implemented at BNC are briefly presented below.

i) Neutron imaging, based on radiography and tomography (RAD Instrument)

ii) Neutron diffraction and scattering

ii.a) Wide-angle neutron scattering (PSD, TOF-ND and MTEST Instruments)

The neutron powder diffraction (NPD) technique focuses on accurate measurements of the positions and intensities of Bragg peaks. The former allows the determination of the lattice parameters, and the latter contain information about the average positions of atoms. Thus, neutron diffraction conveys information on the long-range structure of well-crystallized materials.

Diffuse neutron scattering. Quite often the background between successive Bragg peaks is unstructured, but there exist crystals in which this background is found to exhibit characteristic oscillations and structure, resulting from diffuse scattering, which generally has a strong variation across reciprocal space. Such diffuse scattering contains information about structural fluctuations of structure around the average atomic positions, that, in turn contribute to the short-range structure. Diffuse scattering it thus a tool to analyze the structure of materials on a local scale, allowing to characterize nanomaterials, amorphous materials and poorly crystallized polycrystalline materials. Neutron total scattering experiments, imply data collection corresponding to both Bragg and diffuse scattering.

ii.b) Small-angle neutron scattering (SANS Instrument)

SANS detects the structure of materials at length scales in the range from nano- to micrometres and is typically employed to estimate the size and shape of nano-sized materials.

ii.c) Inelastic and quasi-elastic neutron scattering (TAST/HOLO Instrument)

Inelastic neutron scattering (INS) measurement detect neutrons scattered inelastically at energies close to that of a Bragg peak, yielding information on lattice dynamics (phonons). INS experiments require monochromatisation of the incident or outgoing beam and energy analysis of the scattered neutrons. This can be done either through time-of-flight techniques or with Bragg reflection from an appropriate single crystal. Quasi-elastic neutron scattering (QENS) measures small energy exchanges between diffusing particles and elastically scattered neutrons, which lead to a broadening of the elastic peak and conveys information on the dynamics of loosely bound particles (e.g. diffusing ions), with typical length scales of 0.1-100 nm and timescales of  $10^{-9}$ ,  $10^{-12}$  s.

iii) Neutron reflectivity (GINA Instrument)



Neutron reflectometry consists in delivering a collimated and possibly polarized beam onto the sample surface and measuring the reflected intensity as a function of angle or neutron wavelength. The reflectivity profile conveys information about the structure of the surface, including: thickness, density, and roughness and dynamics of thin films of multi-layered samples, also featuring embedded interfaces.

#### iv) Neutron-based compositional measurements (NAA and PGAA Instruments)

NAA and PGAA are method for quantitative composition analysis of chemical elements, based on nuclear reactions, that exhibit negligible matrix effects, excellent selectivity and high sensitivity, enabling detection of elements in samples of mg mass.

NAA relies on the conversion of stable nuclei of the sample to radioactive ones, followed by the quantification of the reaction products via their gamma radiation.

PGAA is performed by detection of neutron capture prompt gamma rays.

#### *Current state of fuel cell/electrolysis studies*

The main advantages of using neutron scattering methods in FC studies are that, on the one hand, the kinetic energy of neutrons allows to study proton diffusion processes on nanometer length scales and on the other hand, the large penetration through materials allows *operando* observation of processes embedded in functional materials.

Specifically, wide-angle, or neutron powder diffraction (NPD or WANS) at larger angles can resolve atomic distances, while small-angle neutron scattering (SANS) provides insight into mesoscopic length scales above 1 nm, averaged over the sample volume. NPD and SANS can be operated simultaneously: covering atomic to mesoscopic length scales in one experiment has the unique advantage that structural data can be obtained on the same sample under the same conditions. NPS combined with SANS was employed for the study of the arrangement of phosphoric acid in HT-PEMFCs (Holderer 2020).

SANS has been used to probe FC components, to investigate the behaviour of condensed water at different length scales. Specifically, the nanostructure of polymer membranes under various hydration environments was studied *ex-situ* (Nguyen 2017), and ionomer swelling was investigated *in-situ* (Lee 2020). Moreover, SANS allowed to characterise carbon-ionomer interactions in catalyst inks (Shibayama 2014, Balu 2019). In *operando* SANS was used to study the water management running FCs fuel cell (Morin 2016, Martinez 2017). In particular, (Morin 2016) decoupled the measurement of the hydration degree of the ionomer membrane, from that of water accumulation in the GDL and the gas-distribution channels. Interesting opportunities for FC studies are offered by dynamic nuclear polarisation combined with SANS: proton spin polarisation in the sample has been shown – at the moment only in materials that are not directly related to FCs (Noda 2016) – to offer a contrast mode that can be highly diagnostic of polymer structure heterogeneities that can have a strong bearing on the device performance and degradation. In one case, neutron reflectometry was used to study proton diffusion in PEMFC electrode layers (Holderer 2020).

*In-situ* neutron scattering has been in some cases combined neutron imaging: SANS fused with imaging was employed to investigate jointly the water content at macro- and microscales in operating FCs (Iwase 2009) and membrane swelling between ribs and channels (Martinez 2019). Inelastic and quasi-elastic scattering fused with radiography were used to study icing issues in FCs (Biesdorf 2014, Stahl 2016).

The classical approach of FC imaging by neutron radiography and tomography – of course, exploiting the high penetration of neutrons through FC structural materials (graphite, Al, steel), rendering technique especially attractive for in *operando* measurements, and the high contrast for liquid water - is to visualize the water distribution in operating PEMFCs in view of clarifying various aspects of water management, such as: (i) two-phase phenomena in flow channels, pinpointing the effects of geometry (Coz 2016, Meyer 2016) and materials selection (Biesdorf 2015, Forner-Cuenca 2016) as well as characterizing novel metal-foam flow-fields (Wu 2020); (ii) impact of operating conditions (Oberholzer 2013, Gossling 2016) and (iii) degradation modes (Katzel 2016). The range of application of neutron imaging lies between small-scale cells with MEAs of a few cm<sup>2</sup>, to full-size cells of a few hundred cm<sup>2</sup>. Neutron radiography has also been used for the observation of water inside Pt-free electrodes (Babu 2020) in a GDL, in this case exploiting

the dark field technique (Siegwart 2019). More recently, some instrumental development work is starting to appear, in preparation of future tomography of GDLs and catalyst layers.

The lateral resolution for both classical and high-resolution neutron imaging setups (Tremis 2015, Trtik 2016) anti-correlates with the field of view. The introduction of anisotropic setups allowed to achieve a large field of view in one direction and a high resolution in the normal one: a solution that is ideal for cross-sectional FC observation (Oberholzer 2012, Fairweather 2013, Forner-Cuenca 2016, Meyer 2016). To enhance geometrical selectivity the H/D contrast has been exploited, allowing the monitoring of mass transport limitations (Boillat 2013, Arlt 2015). In the radiography mode, currently high lateral and temporal resolutions can be attained, with pixel sizes as low as 30  $\mu\text{m}$  and image acquisition times of 5 s (Chaparro 2020). The radiography mode is the most commonly employed, since tomography requires either total exposure in the range of hours, even though special reconstruction techniques are available, that can employ a limited number of projections. In addition, the lateral resolution in tomography is typically not adequate for accurate observation of GDLs (Takenaka 2011). An important development is to combine *operando* neutron imaging of FCs with other kinds of measurements, such as: local current density and temperature (Meyer 2015).

### **The Instruments of BNC**

Below, we are reporting concise details on the Instruments of BNC accessible under the CERIC-ERIC scheme: (i) brief technical description of each Instrument (more information is available in the "Report on CERIC's - Expert group on batteries" (Bozzini 2020)); (ii) key research activities; (iii) current state of FC studies; (iv) possible adaptation for FC studies; (v) Instrument Scientists' interest in FC studies.

#### **Instrument #1: RAD – Static/dynamic thermal-neutron and X-ray imaging station**

Responsible: Kis Zoltán ([kis.zoltan@energia.mta.hu](mailto:kis.zoltan@energia.mta.hu))

##### *Description of the facility*

RAD is a combined neutron / X-ray radiography / tomography Instrument. The Instrument has been developed for thermal neutron, but fast neutron radiography and tomography have been recently implemented (Zboray 2017): the energy distribution can be tuned with appropriate filters.

The end-station design enables both static and dynamic imaging at video rate. The beam diameter is ca. 200 mm. RAD is also equipped with an X-ray tube (5,300 keV), for complementary imaging.

Two sample stages are dedicated to small and large (up to 250 kg) samples.

The resolution values for neutron and X-ray radiography are in the ranges 0.070, 0.25 and 0.1, 0.2 mm, respectively, with fields of view of 41'34 and 110'93 mm<sup>2</sup>.

Typical exposure times for static imaging are in the range 1,35 s per image, tomography is generally performed with 600, 1000 projections per tomogram. The image acquisition rate for dynamic radiography is 25 frames per second.

##### *Current state of fuel cell/electrolysis studies*

Mainstream research activities are in the fields of: archaeometallurgy, materials for nuclear fuel elements and metallurgy, mainly control of aeronautical castings. Visualization of water condensation within operational fuel cells was successfully demonstrated at RAD. After these tests, the imaging capabilities have been further improved.

##### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The currently available sample stages can host FC experiments, provided the appropriate electrochemical and gas-handling facilities are made available to the Instrument. The Instrument Scientists are in principle interested in FC studies, provided the appropriate human and financial resources are made available either in-house or through collaborations.

#### **Instrument #2: Neutron Diffractometer with a Position Sensitive Detector system (PSD)**

Responsible: Fábrián Margit ([fabian.margit@energia.mta.hu](mailto:fabian.margit@energia.mta.hu))

*Description of the facility*

PSD is a 2-axis diffractometer equipped with a linear position-sensitive detector system, mounted on the diffractometer arm and spanning a scattering angle range of 25° at a given detector position. The sample ambient enables temperature-dependent measurements from room temperature up to 350°C.

*Current state of fuel cell/electrolysis studies*

Research activity is currently centred on the structural investigation of different types of glasses. No FC-related activities have been carried out, so far, at PSD.

*Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

Improvements of the diffractometer would enable FC-related measurements. PSD Staff expresses interest in FC work, but notifies that – in addition to the instrumental improvements mentioned above – dedicated manpower would be needed to develop realistic projects.

Instrument #3: Time-of-flight neutron diffractometer (TOF-ND)

Responsible: Káli György ([kali.gyorgy@energia.mta.hu](mailto:kali.gyorgy@energia.mta.hu))

*Description of the facility*

TOF-ND is a high-resolution time-of-flight powder diffractometer, operating with a thermal neutron beam. The monochromator system is of the chopper-based type. The Instrument covers the d-spacing range 0.5, 2.5 Å with variable band-width and resolution ( $Dd = 0.0015, 0.15$  Å). In the high-resolution an accuracy of  $1.5 \times 10^{-3}$  Å can be achieved with polycrystalline materials and in the low-resolution mode, liquid diffraction can be performed up to a scattering vector of 12.5 Å<sup>-1</sup>. The data acquisition system has been optimized for time-dependent experiments.

*Current state of fuel cell/electrolysis studies*

Main research fields are: structure determination and refinement; peak profile analysis; phase and texture analysis of crystalline materials and diffraction in liquids. One user group carried out a time-dependent *in-situ* experiment trying to detect structural changes under operation. Although the sought-after phases could be observed in the integrated diffractograms, the time-dependent data were not appropriate for evaluation, because of the presence of high amount of hydrogen, and small amount of the matrix. The main problem with this experiment was that the cell, though implementing realistic for practical FC operation, was not optimized for the specific neutron diffraction experiment. The results have not been published.

*Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The development of appropriate electrochemical *in-situ* cells would be an enabling action. The Instrument Responsible considers FCs as a possible program for the Instrument and shows personal scientific interest in the field. An internal research program in collaboration with industrial partners is being elaborated.

Instrument #4: Material Test Diffractometer (MTEST)

Temporary beamline scientists in charge: Alex Szakál ([szakal.alex@ek-cer.hu](mailto:szakal.alex@ek-cer.hu)) and Tamás Veres ([veres.tamas@energia.mta.hu](mailto:veres.tamas@energia.mta.hu))

*Description of facility*

The MTEST thermal neutron diffractometer implements NPD and total scattering analysis in the 2q range 4.5, 142.6° with a resolution of ca. 0.55°. Typical acquisition times for samples of size ca. 1 cm<sup>3</sup> are ca. 6 h for typical amorphous and crystalline samples and ca. 1 day for materials containing appreciable

amounts of hydrogen: smaller samples require longer measurements. The beam size is ca. 10 ´ 40 mm, and it can be adjusted by slits. The beam is monochromatized with 3 crystals that can be changed during data acquisition to optimize the required Q-range and resolution. The available sample environments allow tests in high-temperature (up to 1000°C) and cryogenic (down to 77K) conditions.

#### *Current state of fuel cell/electrolysis studies*

MTEST is a general-purpose instrument and routinely analyses a wide range of solid (powder), liquid and amorphous total diffraction samples in the Bragg and diffuse scattering modes. The structure of anode materials for SOFCs was investigated at room temperature by standard and total-scattering powder diffraction in a beamtime performed in 2019. The results have not been published, at the time of this writing. A beamtime was scheduled for November 2020 to test similar samples in the temperature range from ambient conditions up to 800°C.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

Improved detectors would enable *in-situ* work and shorter acquisition times. MTEST staff is willing to tests of specialized FC sample environments developed by users. Dedicated funding would facilitate this activity. Instrument Scientists express high interest in pursuing FC-related studies.

#### Instrument #5: Small-Angle Neutron Scattering Instrument - "Yellow Submarine" (SANS-YS)

Responsibles: Almásy László ([almasy.laslo@energia.mta.hu](mailto:almasy.laslo@energia.mta.hu)), Len Adél ([len.adel@energia.mta.hu](mailto:len.adel@energia.mta.hu))

#### *Description of the facility*

The SANS diffractometer covers the Q-range 0.003, 0:7 Å<sup>-1</sup>. The beam is monochromatized in a way that allows to select wavelengths between 3 and 12 Å with a precision in the range 12, 30%. Temperature control of the samples is possible in the range 10, 90°C as well as under cryogenic conditions (down to 10K).

#### *Current state of fuel cell/electrolysis studies*

SANS is used in a wide range of fields: defects in materials, multiphase alloys, magnetic materials (an electromagnet can be mounted on the sample-holder), surfactants, colloids and polymers, proteins and biological membranes. SANS actively collaborates with Russian Scientists dealing with polymers for FCs: joint work yielded to publications (Kulvelis 2015, Kulvelis 2016).

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

An *in-situ* cell for FC experiments can be developed rather straightforwardly, if a reasonable amount of manpower and funding is made available. SANS staff manifests interest and availability to develop FC studies and is availability to set up collaborations with users.

#### Instrument #6: Thermal Neutron Three-Axis Spectrometer and Neutron Holographic Instrument (TAST/HOLO)

Responsible: Szakál Alex ([szakal.alex@energia.mta.hu](mailto:szakal.alex@energia.mta.hu))

#### *Description of the facility*

TAST is a highly flexible thermal neutron three-axis spectrometer, operating with independent control in the momentum- and energy-transfer ranges 1.5, 10 Å and 1, 60 meV, respectively, with a resolution of ca. 1 meV and options for filtering off higher-order contributions. TAST can also be used for high-resolution diffraction and inelastic scattering measurements. Monochromatization and energy analysis are performed with appropriate single-crystals. High- and medium-resolution detector options are available. Two sample-holder options are available: a Eulerian Cradle and a tilt table that can host objects of mass up to 100 kg. The TAST instrument can also be used for atomic-resolution neutron holography: this approach is based on the recording of the interference of neutron waves coherently scattered by atoms located on a crystal

lattice with an appropriate reference wave, generally from a source of plane neutron waves located outside the sample [cser2004atomic]. The interference between the undisturbed and the scattered fractions of the neutron wave field is monitored by strongly neutron-absorbing nuclei, which are present in the crystal lattice that is to be imaged. Acting as point-like detectors. Detection can be performed in in neutron- or gamma-ray modes.

#### *Current state of fuel cell/electrolysis studies*

The scientific activities of TAST are centred on the measurement of phonon and magnon dispersion in single crystals, and to measure the phonon density of states in hydrogen-containing materials. No experiments related to FCs have been carried out at TAST at the time of this writing.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

A special sample environment would be needed for FC work and the TAST Staff is available to collaborate with external group to set up a project in the field. In principle, the Instrument Responsible is interested in FC studies, but dedicated manpower would be needed to make the project feasible.

#### Instrument #7: Neutron Reflectometer with Polarized Beam Option (GINA)

Responsible: Dániel G. Merkel ([merkel.daniel@energia.mta.hu](mailto:merkel.daniel@energia.mta.hu))

#### *Description of the facility*

GINA is a constant-energy angle-dispersive, vertical-sample instrument. A focusing graphite monochromator provides unpolarized and polarized neutron beams with wavelength optimized at 4.67 Å. The available Q-range is 0.005 (resolution 10%) , 0.25 (resolution 2%) Å<sup>-1</sup>. The beam scattered by the sample can be spin-analyzed. The scattering plane is horizontal and the samples have to be placed in the vertical position. The available sample environment components include: permanent-magnet sample stage for large samples, cryostat (20 , 300 K, operating in vacuo), electromagnet (up to 0.55 T, compatible with cryostat), water-cooled Helmholtz coils (up to 35 mT) and thermostated solid/liquid cell (±0.1K). Neutron scattering by air can be minimized with a mountable flight tube.

#### *Current state of fuel cell/electrolysis studies*

Studies at GINA chiefly revolve around structural determination of metallic multilayers and heterostructures, including magnetic ones. Recently, soft matter research topics have been faced: biological membranes and self-assembly of nanoparticles in solutions. The GINA group also operates and BME for material preparation and a Mössbauer spectrometer. FCs related experiments have never been run at GINA, so far.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The current configuration of GINA is suitable for FC-related studies, though with some limitations. On the one hand, the depth resolution matches well the scales relevant to electrocatalyst studies, but, on the other hand the brightness of the neutron source is not optimized for fast time-dependent studies, samples of dimensions smaller than 1 cm<sup>2</sup> and off-specular scattering. In addition, the reflectometer is of the fixed-l type and is not suitable for time-slicing (i.e. a full reflectogram must be recorded at a particular state). Even though GINA currently has no electrochemical expertise, cells for neutron reflectivity have been described in the literature, that can be straightforwardly adapted for FC work at BNC. The GINA Staff is available to develop projects in the field of FCs: a first concrete step could be to finalize the construction of a dedicated electrochemical cell, a preliminary design of which is already available.

#### Instrument #8: Neutron Activation Analysis (NAA)

Responsible: Katalin Gmélíng ([gmeling.katalin@energia.mta.hu](mailto:gmeling.katalin@energia.mta.hu))

#### *Description of the facility*



Samples for NAA are irradiated with neutrons in the core of the reactor: two dedicated channels are available for short- and long-time irradiation. Three low-background gamma-spectroscopic counting chambers are available for the measurement of the gamma-rays emitted from the samples. NAA is complementary to PGAA (see Section 9 below) and combined measurements are sometimes carried out. At variance with PGAA, NAA analyses are destructive and activated samples have to be discarded after analysis. Nevertheless, the detection limit of NAA is far better than that of PGAA. The Instrument has just undergone major refurbishment actions and is planned to resume operation in January 2021.

#### *Current state of fuel cell/electrolysis studies*

NAA is a general-purpose instrument for elemental analysis. At BNC the method is most frequently used for the compositional analysis of trace impurities in raw materials for photovoltaic devices. NAA does not report any previous experience with FC-related samples.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The analysis setup is adequate for *ex-situ* compositional analyses without space resolution of samples of FC materials, electrocatalyst in particular. In fact, ultra-precise quantification of metal content of fuel-cell cathodes and anodes is possible, as the organic matrix does not produce any background. The Instrument Responsible showed interest in developing projects specifically focused on FC science and technology.

#### Instrument #9: Prompt Gamma Activation Analysis (PGGA)

Responsible: Szentmiklósi László ([szentmiklosi.laszlo@energia.mta.hu](mailto:szentmiklosi.laszlo@energia.mta.hu))

#### *Description of the facility*

At PGAA, samples are irradiated with thermal neutrons are brought from the reactor to the experimental positions by a neutron guide, designed to minimize background from the core. For better signal-to-noise ratio, the beam can be modulated with a chopper. The beam can be collimated to a maximum cross-section of 2'2 cm<sup>2</sup> and a series of collimators can tailor the beam. The detection system is designed in a way such that also scattered g-rays can be collected. The targets are mounted on thin Al frames by Teflon strings. An automated sample changer with 16 positions is available and the sample chamber can be evacuated or filled up with gases to decrease beam-induced background.

#### *Current state of fuel cell/electrolysis studies*

In addition to general analytical work, in part dedicated to catalysis, the key ongoing project in this moment is on circular economy and deals with the recycling and recovery of valuable/harmful/toxic materials from end-of-life products. PGAA is one of the very few techniques capable of directly quantifying hydrogen *in-situ* and it would be perfectly fit for FC studies. The instrument Scientists have measured the compositions of Nafion membranes as well as the Pt content of commercial FC anode and cathode materials. PGAA is not capable of resolving the hydrogen profile through a Nafion membrane, but in principle it should be suitable for *operando* studies of FC stacks.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

Development of a dedicated sample stage would favor FC work. PGAA Scientists is fully open to initiatives and collaborations in the field of FCs and are willing to support related actions with their analytical and instrumental skills.

## **2.5. Italy**

### **2.5.1. SISSI - Synchrotron Infrared Source for Spectroscopy and Imaging & SISSI-offline (Trieste, Italy)**

Responsible: Lisa Vaccari ([lisa.vaccari@elettra.eu](mailto:lisa.vaccari@elettra.eu)) and Giovanni Birarda ([giovanni.birarda@elettra.eu](mailto:giovanni.birarda@elettra.eu))

*Description of the facility*

The SISSI infrared beamline at Elettra extracts the IR and visible components of synchrotron emission to perform spectroscopy, microspectroscopy and imaging. It is formally divided into two branchlines: the Chemical and Life Sciences branchline (SISSI-Bio) and the Material Science branchline (SISSI-Mat). Radiation for the SISSI beamline is collected from a bending magnet with a wide acceptance angle and comprises a broad range of emissions. The extracted radiation is manipulated with an optical system in UHV, allowing minimizing the aberrations deriving from the transfer optics due to the wide emission angle. Finally, appropriate mirrors deviate the IRSR beam towards the two branchlines and focus it on CVD diamond windows, which are the last UHV component.

The Material Science branchline is equipped with a spectrometer for spectroscopy and spectromicroscopy measurements over a broad spectral range. In particular, the possibility to mount different detectors on the infrared microscope allows exploiting a diffraction limited beam from the visible down to the terahertz. The branchline is also equipped with cryostats and diamond anvil cell, thus allowing to explore the behavior of matter at extreme conditions of temperature and pressure.

The Chemical and Life Sciences branchline is optimized for FTIR spectroscopy, microscopy, and imaging in the Mid infrared. The newly installed interferometer with full range FIR-MIR accessories guarantees the possibility to explore the FIR regime. The BioChem branchline offers full support for chemical and biomedical applications, and opportunities for cultural heritage, geological science and biophysics as well.

*Current state of fuel cell/electrolysis studies*

So far, SISSI has no experience in electrochemical experiments involving fuel cell and electrolysis materials.

*Interest of the facility in prospective fuel cell/electrolysis studies*

The beamline staff is willing to extend the beamline activities to topics related to electrochemistry and energy conversion. They are aware that infrared spectroscopy and spectro-microscopy have already been used to investigate electrochemical reactions and electrified interfaces at the Infrared Beamline in Canada at CLS (Rosendahl, Borondics et al. 2011, Rosendahl, Borondics et al. 2013, Morhart, Quirk et al. 2016, Lardner, Tu et al. 2017). In particular synchrotron-sourced infrared radiation allowed to map the electrochemical activity of a PtNi alloy towards methanol oxidation, by measuring the rate of CO<sub>2</sub> production at variable positions along the alloy concentration gradient using an infrared microscope (Tu, Lardner et al. 2016). This kind of study would be of great interest to study the electrocatalytic activity of catalysts towards the relevant reactions taking place in fuel cell and electrolyzers.

**2.5.2. IUVS - Inelastic UltraViolet Scattering and IUVS-offline (Trieste, Italy)**

Responsible: Barbara Rossi ([barbara.rossi@elettra.eu](mailto:barbara.rossi@elettra.eu))

*Description of the facility*

The IUVS beamline is dedicated to the study of inelastic scattering with ultraviolet radiation, in a time-space domain not accessible at present by other facilities. The peculiarity of IUVS is the specific kinematic region that can be investigated. IUVS beamline delivers photons with incident energy between 5 and 11 eV. The incident photons that are inelastically diffused by the sample can be analyzed by exploiting the two different and complementary experimental set-up available on the beamline, i.e. UV Brillouin and UV Resonant Raman scattering instruments, in order to probe both the acoustic and optical phonons propagating in the system. This allows to acquire information about the structure and dynamics of the constituent matter over different length scales through the analysis of its collective and molecular vibrations.

The almost-backscattering configuration of Brillouin setup, with scattering angle  $\theta$  of 178 degree, allows an exchanged momentum range of  $2 \times 10^{-2}$ – $2 \times 10^{-1} \text{ nm}^{-1}$ , corresponding to 10–1000  $\mu\text{eV}$  scattered energy allows to investigate a kinematic region not accessible at present by other experimental techniques as Brillouin scattering with visible light, X-Ray scattering and neutron scattering.

The experimental setup that enables to perform UV Resonant Raman spectroscopy using synchrotron radiation in the range of wavelengths 200–270 nm provides a fine-tunable source in the deep-UV for mapping a wide resonance landscape range in different samples, from nanostructures and strongly correlated materials to biophysical and biochemical systems.

#### *Current state of fuel cell/electrolysis studies*

So far, no direct experience of the beamline scientist with energy conversion studies. However, she raised the interest of the SR-UVR technique as potentially useful for fuel cell, electrolysis and CO<sub>2</sub> electro-reduction. Currently there are no potential industrial users.

#### *Interest of the facility in prospective fuel cell/electrolysis studies*

As a perspective the study of nanocomposite ion exchange membranes and hydrogen bonds in between their components (e.g. nanostructured reinforcements and ionomer matrix) has been highlighted.

### **2.5.3. Materials Characterisation by X-ray Diffraction (MCX) (Trieste, Italy)**

Responsible: Jasper Rikkert Plasier ([jasper.plaisier@elettra.eu](mailto:jasper.plaisier@elettra.eu))

#### *Description of the facility*

The MCX beamline is a general-purpose X-ray diffraction beamline with a large useful energy range from 6 to 20 keV and equipped with a four-circle goniometer, allowing a wide range of non-single crystal diffraction experiments: grazing angle diffraction and reflectivity, residual stress and texture analysis, phase identification and structural studies and kinetic studies.

Systems that can be investigated vary from organic and inorganic thin films, to thermally and/or mechanically modified surfaces of mechanic components, to polymers, catalysts and highly disordered materials in the form of films, powders, fibres. The research carried out at MCX concerns fields related to materials science, archaeometry, geophysics, solid state and superconductors physics, catalysis, solid state chemistry, energy materials.

#### *Current state of fuel cell/electrolysis studies*

Even though the instrument is used for battery research, the research on fuel cell technologies is underrepresented. An exception is a long-term collaboration with a group of users that is working on the structural characterisation of SOFC electrolytes. However, their interest is rather academic. Several publications have been published on this topic (Artini, Pani et al. 2014, Artini, Pani et al. 2016, Artini, Carnasciali et al. 2017, Artini, Carnasciali et al. 2018, Artini, Gigli et al. 2019).

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

XRD is one of the standard characterisation techniques used in fuel cell research as structural characterisation is an important part of research into the stability and activity of the materials. Therefore, there is a large potential to further exploit this instrument of FC research. Currently the instrument is rather underused in this respect.

Given the ability to perform grazing incidence measurements, the instrument is ideally positioned for the investigations of model catalyst surfaces. This is perfectly complementary to the CERIC-ERIC XPS and SAXS instruments and bundling the XRD with those techniques would provide added value for CERIC-ERIC offering for FC community.

Further, standard powder diffraction experiments can be also performed, therefore applied nano-materials can be also characterized without any problems. While *ex-situ* characterisation is a standard technique at

the instrument it is advised that simple electrochemical liquid cell is developed which can be used for *in-situ* structural characterisation of catalyst materials during applied potentials or during accelerated stress tests. This kind of information is invaluable not only for the academic users but can be also exploited by industrial users. Such *in-situ* experiments would exploit the high energy range of the beamline (around 20 keV) which is sufficient to penetrate small electrochemical liquid cell. Various standards cell designs in both transmission and grazing incidence geometry can be used.

#### **2.5.4. Electron spectroscopy for chemical analysis (ESCA) microscopy (Trieste, Italy)**

Responsible: Luca Gregoratti ([luca.gregoratti@elettra.eu](mailto:luca.gregoratti@elettra.eu))

##### *Description of the facility*

The ESCA microscopy beamline hosts a Scanning photoelectron microscope (SPEM), combining chemically surface sensitivity with high spatial resolution. The spot size can be defined down to 120 nm and energy sensitivity is within 180 meV at 90-1800 eV energy range. The high-flux third-generation X-ray source feeding the line, enables space-dependent quantitative and qualitative chemical characterisation of complex materials with micrometre spatial resolution. The SPEM can operate in two modes: imaging and spectroscopy. In the former, the sample surface is mapped by scanning the sample across to the focused photon beam and collecting photoelectrons with a selected kinetic energy. The latter is photoelectron spectroscopy, obtained by analyzing the photoelectrons emitted from a microspot.

Typical experiments include chemical and electrochemical reactions; mass-transport processes, leading to lateral changes in the composition; morphology and electronic properties of materials. A special cell has been recently developed for Near Ambient Pressure SPEM.

##### *Current state of fuel cell/electrolysis studies*

The instrument scientists have a specific experience in this field. With ESCA microscope they started more than 15 years ago to run experiments on solid oxides fuel cells. More recently characterisations on batteries and electrochemical devices used as sensors have been performed as well. The instrument allows chemical and electronic surface characterisations at submicron scale *ex-situ/in-situ/operando* also at near ambient pressure conditions. However, no proposals came through the CERIC-ERIC. Three publications in the field of FC have been published in last 5 years (Calvillo, Valero-Vidal et al. 2016, Bozzini, Previdi et al. 2019, Bozzini, Amati et al. 2020).

##### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

SPEM techniques are well established in the field and have been proven to be one of the workhorses in determining the spatial inhomogeneities of the fuel cell materials. The instrument is already to some extent adapted to this kind of work and can be further developed. Mainly dedicated in situ electrochemical cells are available for gas-solid interface, but cells dedicated for studies of liquid-solid interface are missing. However, given the great overlap with other CERIC-ERIC instruments, it is advised that a dedicated liquid cell is developed with the help of UK, Prague facilities which already have some experience in this direction. Also, the FC work is currently user driven at this instrument. So it is vital that the users are further encouraged to use this instrument for their research by developing strong user/instrument incentive (grant, PhD position,...).

#### **2.5.5. Material Science Beamline MBS (Elettra, Trieste)**

Responsible: Nataliya Tsud ([tsud@mbox.troja.mff.cuni.cz](mailto:tsud@mbox.troja.mff.cuni.cz)) and Tomas Skala ([tomas.skala@elettra.eu](mailto:tomas.skala@elettra.eu))

##### *Description of the facility*

The MSB is a versatile beamline suitable for experiments in materials science, surface physics, catalysts and organic molecules on various surfaces, built-in cooperation between the Institute of Physics of the

Czech Academy of Sciences and Sincrotrone Trieste. The tunability of the photon energy over a wide range (22 – 1000 eV), with mainly linearly polarised light from a bending magnet source, offers classical UPS and XPS with high energy resolution and tunable excitation energy for the best photoionisation cross-sections. The beamline also allows resonant photoemission (RESPES) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopies in TEY mode. Sample rotation about two axes allows angle-resolved photoemission studies.

Some equipment currently used for electrocatalysis and sensors are available on the beamline and shared with the NAP-XPS laboratory in Prague. In particular, the electrochemical cell available to the user community has been developed in cooperation with the NAP-XPS laboratory (vide supra).

#### *Current state of fuel cell/electrolysis studies*

The instrument is very active in research of (electro)catalysts used in various types of fuel cells and electrolyzers. In last 5 years 26 publications have been published on this topic (Dvořák, Farnesi Camellone et al. 2016, Kettner, Ševčíková et al. 2016, Khalakhan, Vorokhta et al. 2016, Kúš, Ostroverkh et al. 2016, Lykhach, Figueroba et al. 2016, Monai, Montini et al. 2016, Neitzel, Figueroba et al. 2016, Neitzel, Johánek et al. 2016, Ševčíková, Szabová et al. 2016, Vorokhta, Khalakhan et al. 2016, Khalakhan, Vorokhta et al. 2017, Lykhach, Bruix et al. 2017, Artiglia and Agnoli 2018, Dvořák, Szabová et al. 2018, Faisal, Bertram et al. 2018, Faisal, Stumm et al. 2018, Lykhach, Faisal et al. 2018, Schwarz, Faisal et al. 2018, Brummel, Lykhach et al. 2019, Lykhach, Kubát et al. 2019, Bertram, Prössl et al. 2020, Brown, Vorokhta et al. 2020, Brown, Vorokhta et al. 2020, Khalakhan, Vega et al. 2020, Lykhach, Skála et al. 2020).

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

This instrument is well known for the synchrotron XPS characterisation of (electro)catalyst materials. However, the involvement of users should be further promoted as the majority of publications comes from few user groups. Combined offer with the XAS beamlines and elastic scattering instruments (XRD, SAXS, SANS) should be made so the users can fully exploit CERIC facilities.

It is also advised that the further development of *in-situ* electrochemical cells will be promoted so the instrument will be able to also provide critical data regarding the electronic structure of materials in their native environment. This development should be done with the collaboration with other CERIC facilities.

### **2.5.6. X-ray Absorption Fine Structure (XAFS) beamline (Elettra, Trieste)**

Responsible: Giuliana Aquilanti ([giuliana.aquilanti@elettra.eu](mailto:giuliana.aquilanti@elettra.eu))

#### *Description of the facility*

The XAFS beamline is dedicated to X-ray Absorption Spectroscopy. It is installed on a bending magnet source and it was designed to cover a wide energy range, from 2.4 to 27 keV. Being site-selective and having local character, this technique provides information at the same time on the electronic structure and on the local environment of the absorbing atom.

Different collection modes are available. Transmitted photons are measured using three ionization chambers in series, allowing to record simultaneously the XAS spectrum from the sample and from a reference. A Silicon drift detector is used to collect the fluorescence photons, in case of diluted or too concentrated samples. Moreover, a converter total electron yield can allow collecting the secondary electrons and therefore to have access to the surface information.

Several sample environments are available (including furnace, liquid-N<sub>2</sub> cryostat and cells for liquid samples). In this way, XAFS beamline meets the needs of a large number of researchers in the area of conventional x-ray absorption spectroscopy.

#### *Current state of fuel cell/electrolysis studies*

The beamline is very active in a broad range of materials science, including (heterogeneous) catalysis and battery research. However, we have not been able to identify papers on fuel cell or electrocatalysis studies. The website does mention a research highlight (in Italian) on participation in the CERIC-CEROP project



(funded 2016) which aimed at the *operando* characterisation of anodic catalysts with reduced Pt content. Unfortunately, no further details could be found or were provided.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The accessible energy range as well as the advanced experience of the beamline in *operando* catalysis and battery studies, makes the beamline very suitable for state-of-the-art *operando* electrocatalysis and electrolysis studies on transition metal catalysts in liquid environments. Currently, the beam line does not seem to have any electrochemical equipment available and rely on users to bring their own. To enable fuel cell related work, the beamline would definitely benefit from having available suitable *operando* spectro-electrochemical fuel cell set-ups (several designs available for purchase to adjust to the beamline and several designs presented in literature), including the required associated potentiostats, etc. (See also other XAS beamlines in this document).

### **2.5.7. Soft X-ray Transmission and Emission Microscope TwinMic (Elettra, Italy)**

Responsible: Alessandra Gianoncelli ([alessandra.gianoncelli@elettra.eu](mailto:alessandra.gianoncelli@elettra.eu))

#### *Description of the facility*

TwinMic is a soft-X ray microscope that integrates the advantages of complementary scanning and full-field imaging modes into a single instrument. The uniqueness of the X-ray microscopy results from the combination of different features:

- 3.3 The shorter wavelengths allow higher optical resolution compared to visible light microscopy;
- 3.3 The high X-ray penetration provides deeper insight into samples, avoiding in many cases specimen slicing, as typically required for TEM;
- 3.3 The combination with X-ray spectroscopy allows characterisation of the electronic structure of the atoms present.

The light source is a 1m short undulator, featuring a brilliance similar to that of conventional undulators, but higher in angular divergence, highly suited for the twin microscope concept and facilitating the combination of complementary imaging and spectromicroscopy modes. The beamline is equipped with a variable-angle plane grating monochromator, with high energy resolution in the range 400-2200 eV. The end station TwinMic has the unique capability to operate both as a transmission X-ray microscope (TXM) and as a scanning TXM (STXM). Both modes can be employed to implement coherent diffractive imaging approaches.

TwinMic combines high lateral resolution with X-ray absorption contrast, in particular between organic matter and water that allows imaging of specimens in their natural liquid environment. The highest lateral resolution can be achieved with the full-field imaging mode, which is currently about 20 nm using special objective lenses. Other imaging modes require optimisation of X-ray intensity and chemical sensitivity, and generally allow micrometric and sub-micrometric lateral resolution. Typical research fields are: biotechnology; nanotechnology; environmental science and geo-chemistry; clinical and medical applications; novel energy sources; biomaterials and cultural heritage.

#### *Current state of fuel cell/electrolysis studies*

TwinMic has been hosting users and collaborating on projects in the fields of energy research over the last 10 years, including a recent industrial collaborator. There is considerable emphasis on battery research, but also includes fuel cells, electrocatalysis and deposition and corrosion.

A research highlight is for example the use of *in-situ* X-ray imaging and spectro-microscopy to study metal corrosion products in PEMFCs (Bozzini, Gianoncelli et al. 2011). Other examples include *in-situ* and *operando* studies looking at the electrodeposition dynamics and morphology (Bozzini, Kourousias et al.

2017, Bozzini, Kourousias et al. 2017), as well as analysing speciation and morphology of reaction and corrosion products in FCs (Bozzini, Abyaneh et al. 2012, Bozzini, Gianoncelli et al. 2013).

*Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The TwinMic staff is already active in energy research and in fuel cell research in collaborative projects. They are highly interested in developing and implementing electrochemical wet cells for fuel cell studies in their instrument, having a lot of experience in designing suitable cells for other applications.

## **2.5.8. Nanospectroscopy Beamline (Elettra, Trieste)**

Responsible: Andrea Locatelli ([andrea.locatelli@elettra.eu](mailto:andrea.locatelli@elettra.eu))

*Description of the facility*

The Nanospectroscopy beamline operates a state-of-the-art spectroscopic photoemission and low energy electron microscope (SPELEEM). This instrument offers a wide range of complementary methods providing structural, chemical and magnetic sensitivity. The lateral resolution of the microscope currently approaches few tens nm. The microscope is served by a high photon flux beamline, which can deliver elliptically polarized photons in the range 50 eV to 1000 eV.

A small preparation chamber allows simple treatments such as annealing and exposure to gas. A small heating facility allows annealing and flash up to temperatures of about 2000 K. An Ar ion gun facing the sample is provided for sputtering. The main chamber is equipped with 6 ports for e-beam evaporators, and 1 port for illuminating the sample with Hg-lamp. Available facilities are a gas line with precision leak valves, e-beam evaporators (Focus - Omicron GmbH), a quadrupole mass spectrometer, a magnetization stage, and a sample parking stage.

Research takes place in fields such as surface physics and chemistry, magnetism, materials science and nanotechnology, exploiting the high surface, chemical and electronic structure sensitivity of core level and valence band XPEEM.

*Current state of fuel cell/electrolysis studies*

The beamline has no experience with fuel cell or electrocatalysis/electrolysis studies. There is an ongoing collaboration on the morphology and structure of  $\text{LiCoO}_2$  films as a function of Li content, i.e. spatially resolved XAS on battery type materials.

*Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The beamline scientist states that there is a potential interest. In principle, a special sample cartridge could be designed and build, allowing the application of voltages to a specially designed sample. Even if it is likely impossible to perform *operando* XPEEM (i.e. while applying voltages), the surface chemistry before, after and at various stages of the reaction could as such be characterised.

## **2.5.9. Gas Phase Photoemission (GAPH) Beamline (Elettra, Trieste)**

Responsible: Kevin C. Prince ([kevin.prince@elettra.eu](mailto:kevin.prince@elettra.eu))

*Description of the facility*

The Gas Phase Photoemission (GAPH) beamline is specifically devoted to research on gaseous systems. GAPH offers a multi-technique approach for the investigation of electronic properties of free atoms, molecules and clusters in the photon energy range 13-900 eV.

The broad energy range, the high resolving power and flux together with the purpose-built end-stations, make this facility ideal for investigating the spectroscopy and dynamics of basic processes like inner-shell and multiple excitations and ionization, as well as for characterizing key processes relevant to several areas of science and technology (for example atmospheric chemistry, material science and biomedical sciences).

*Current state of fuel cell/electrolysis studies*

The beamline is not involved in fuel cell research. The low energy and the dedication to gas-phase processes do not allow studies on solid electrodes or fuel cell reactions and processes.

### **2.5.10. Band Dispersion and Electron-Phonon Coupling (BaDEIPh) Beamline (Elettra, Trieste)**

Responsible: Luca Petaccia ([luca.petaccia@elettra.eu](mailto:luca.petaccia@elettra.eu))

*Description of the facility*

The BaDEIPh beamline provides photons in the energy range 4.6-40 eV with high flux, high resolving power and horizontal-vertical linear polarization. The beamline serves an end station to perform primarily high-resolution angle-resolved photoemission spectroscopy (ARPES) experiments in the low photon energy regime. Due to the low photon energy, the surface preparation and the crystallinity of the sample are crucial. Research takes place in fields related to condensed matter and surface physics, materials and nano-science.

*Current state of fuel cell/electrolysis studies*

The beamline is not involved in fuel cell research. Due to the extreme low photon energy and thereby high surface sensitivity, (*ex-situ*) electrodes are not suitable candidates for surface studies.

### **2.5.11. Spectromicroscopy Beamline (Trieste, Italy)**

Responsible: Alexey Barinov ([alexey.barinov@elettra.eu](mailto:alexey.barinov@elettra.eu))

*Description of the facility*

The beamline houses unique microscope designed for studies of the local band structure of materials. A low photon energy beam (below 100 eV) is focused into a sub-micrometre spot and electrons arising from the photoemission process are collected and analysed in terms of their angular and energy distributions (ARPES).

The final focusing is obtained by multilayer-coated optics of Schwarzschild objectives. The use of multilayers required for high reflectivity at a certain wavelength restricts the photon energy range available after the monochromator (20 - 200 eV) to specific narrow lines. Currently the beamline is equipped with two Schwarzschild objectives designed for 27 and 74 eV of photon energy.

ARPES is then performed by means of an internal moveable electron energy analyser mounted on precision two axes goniometer setup. The sample can be measured in the temperature range of 40-470 K and the sample focusing and imaging are performed thanks to the XYZR scanning stage on which the sample manipulator is mounted.

Spectro-microscopy is devoted to a user community working in the fields of surface and material science (strongly correlated materials, topological insulators, etc.) with particular emphasis on electronic structure phenomena such as electronic phase transitions and electronic structure of small – down to sub micrometre size – objects.

*Current state of fuel cell/electrolysis studies*

The beamline staff has not indicated any interest. The beamline works in Ultra High Vacuum environment, severely limiting *operando* fuel cell studies. Flat surface solid samples can be mounted and potential applied. This would potentially allow surface studies of model electrodes as a function of potential (in the absence of electrolyte).

### **2.5.12. X-Ray Diffraction 1 (XRD1) beamline (Trieste, Italy)**

Responsible: Maurizio Polentarutti ([maurizio.polentarutti@elettra.eu](mailto:maurizio.polentarutti@elettra.eu))

#### *Description of the facility*

The XRD1 beamline has been designed in collaboration with the Istituto di Cristallografia - CNR primarily for macromolecular crystallography, but the characteristics of the beamline permit to perform a wide variety of experiments. The light source is a multipole wiggler with a useful range from 4 to 21 keV, allowing the optimization of the anomalous signal of several heavy atoms (up to the calcium edge), and offering the enhancement of the Sulphur anomalous signal. Moreover, such wide energy range allows both reflection and transmission geometry, for a tunable penetration depth.

The experimental setup consists in a Huber goniometer with  $\theta$  geometry fully controllable from remote. An Oxford Cryostrem 700 allows cooling the sample in the temperature range 80–400 K. Two XRD detectors are available. A classical MAR165 with 2.5 s readout is offline, but still working. A 2D PILATUS detector with 3 ms readout at 12 Hz frame rate, allows following structural transition, preferential orientation and degree of order in the material. In addition, a Si drift detector for fluorescence measurements is installed. A high-throughput data acquisition is achieved using the mechanical robot developed on the beamline to change automatically the capillaries under the beam. The beamline hosts small molecules, protein crystallography, powder diffraction, high-pressure physics and solid-state experiments.

#### *Current state of fuel cell/electrolysis studies*

The XRD1 beamline has been highly demanded by the CERIC-ERIC users, but not for FC research.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The instrument can be used for *ex-situ* characterisation of FC materials. But given the lack of interest from the beamline responsible further development for the FC community is not foreseen.

### **2.5.13. SuperESCA beamline (Trieste, Italy)**

Responsible: Luciano Lizzit ([luciano.lizzit@elettra.eu](mailto:luciano.lizzit@elettra.eu))

#### *Description of the facility*

The SuperESCA beamline implements high-resolution core-level photoemission spectroscopy (HR-XPS). This method allows in-depth investigations on the electronic and structural properties of a variety of samples, ranging from single crystals to thin films and nanostructured materials. The beamline has been designed primarily for soft X-ray photoemission experiments on surfaces. SuperESCA combines high-resolution capabilities with a high flux of linearly polarized photons in the 90 to 1500 eV range, allowing to obtain high-resolution spectra also for low-density systems and to follow in real-time surface processes and reactions. Moreover, the beamline has XPD capabilities.

#### *Current state of fuel cell/electrolysis studies*

No studies in the field of fuel cells have been reported by the beamline responsible.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The instrument can be used for *ex-situ* characterisation of FC materials. The beamline staff would be interested in developing electrochemical cells and instrumentation, in particular with e-transparent graphene window. This would open up further possibilities for the CERIC-ERIC users.

## **2.6. Poland**

### **2.6.1. Cryo Electron Microscopy (Krakow, Poland)**

Responsible: Sebastian Glatt ([sebastian.glatt@uj.edu.pl](mailto:sebastian.glatt@uj.edu.pl)), Michał Rawski ([michal.rawski@uj.edu.pl](mailto:michal.rawski@uj.edu.pl)), Paulina Indyka ([paulina.indyka@uj.edu.pl](mailto:paulina.indyka@uj.edu.pl))

#### *Description of the facility*

The Thermo Scientific™ Krios™ G3i Cryo-Transmission Electron Microscope (Cryo-TEM) enables researchers to study matter at molecular level with resolution of 2 Å. Its highly stable 300 kV TEM platform and cryogenic sample manipulation robot are designed for automated applications, such as single-particle analysis and cryo-tomography.

#### *Current state of fuel cell/electrolysis studies*

The laboratory focuses on collecting structural biology data for users, which are mainly molecular biologists and biochemists, therefore it has no experiences in the field of energy conversion. It works in close contact with biotech and pharmaceutical industries.

#### *Interest of the facility in prospective fuel cell/electrolysis studies*

This facility mainly deals with biological samples. The scientists do not think that it can be useful for the study of energy materials. However, cryo-electron microscopy may give the possibility to investigate the structure and ionomer distribution in catalyst layers and membranes for fuel cells and electrolyzers. e. g. (Guo, Pan et al. 2021).

### **2.6.2. Photoemission Electron Microscopy / X-ray Absorption Spectroscopy beamline (Solaris, Krakow)**

Responsible: Marcin Zajac ([mar.zajac@uj.edu.pl](mailto:mar.zajac@uj.edu.pl))

#### *Description of the facility*

The PEEM/XAS beamline is dedicated to microscopy and spectroscopy in the absorption of soft X-rays (200–2000 eV) and is equipped with two end-stations: a photoemission electron microscope (PEEM), and a universal station for X-ray absorption spectroscopy (XAS) (<https://synchrotron.uj.edu.pl/documents/1457771/114907010/linia-1-EN.pdf>).

The PEEM end-station is a fully equipped “surface science laboratory”. It includes a load-lock and an entrance chamber for fast sample transfer from air into the ultrahigh vacuum (UHV) environment, a preparation chamber, the main microscopic chamber.

The XAS end-station is a UHV system equipped with two chambers (one for spectroscopy and other for preparation). Total electron yield, partial electron yield and total fluorescence yield detectors are available. The preparation chamber includes LEED and Auger spectrometers, several evaporation sources, an ion sputtering source, and a gas dosing system, thermal annealing process up to 2000 K. An additional evaporation source is mounted in the main chamber for real-time microscopy during the deposition.

#### *Current state of fuel cell/electrolysis studies*

There is currently no FC research taking place on the beamline, nor is interest indicated by the beamline staff. The low X-ray energy complicates *operando* experiments and would limit the research to *ex-situ* studies on electrode surfaces.

### **2.6.3. Ultra-Angle Resolved Photoelectron Spectroscopy beamline (Solaris, Krakow)**

Responsible: Jacek Kolodziej ([jacek.kolodziej@uj.edu.pl](mailto:jacek.kolodziej@uj.edu.pl)), Natalia Olszowska ([natalia.olszowska@uj.edu.pl](mailto:natalia.olszowska@uj.edu.pl))



*Description of the facility*

The UARPES beamline is an experimental installation for studies of the electronic band structure of solid surfaces. The beamline is designed for the energy range 8 – 100 eV, providing high photon flux, high resolution, and variable polarization, with minimized harmonic contamination. Techniques available are Angle-resolved photoelectron spectroscopy (ARPES) at sample temperature 8–500 K, low energy electron diffraction (MCP-LEED), Auger electron spectroscopy (AES).

Many recent advances in materials science have been enabled by better understanding of the electronic structure of complex systems, gained due to ARPES studies. Examples include advances in fields such as: high-temperature superconductivity, topological insulators, graphene physics.

*Current state of fuel cell/electrolysis studies*

No FC, or FC-related studies have been performed. The beamline operates at very low X-ray energies required UHV. Some information on electronic band structure of model single crystal surfaces might be obtained. The beamline staff has not indicated interest.

## 2.7. Romania

As part of the National Institute of Materials Physics, the Laboratory of Atomic Structures and Defects in Advanced Materials (LASDAM) has a strong expertise in solid-state physics and materials science, with a research activity related to the study of the physical properties (structural, optical, electrical) of advanced materials (dielectrics, semiconductors, alloys, ceramics) for various applications (semiconductor technology, gas sensing, radiation detectors, telecommunications).

The centre is committed to materials characterisation by advanced microstructural and spectroscopic techniques, such as analytical TEM and EPR spectroscopy. Therefore, the scientists approach a wide variety of materials, depending on the profile of the groups they collaborate with: from nanoparticles to thin films, ceramics and alloys for various applications, including energy conversion and storage. The laboratory has collaboration with academic users but not with industry. In the frame of CERIC, they are collaborating with Institute of Physical Chemistry in Bucharest (Romania), Charles University in Prague (Czech Republic), University of Minho (Portugal), Gdansk University of Technology (Poland), University of Bologna (Italy) on topics related to fuel cells and electrolysis.

### 2.7.1. High Resolution Transmission Electron Microscopy at LASDAM (Magurele, Romania)

Responsible: Corneliu Ghica ([cghica@infim.ro](mailto:cghica@infim.ro))

*Description of the facility*

The HRTEM is a multifunctional tool designed for the research and characterisation of advanced materials, used for conventional transmission electron microscopy, high-resolution transmission electron microscopy, electron tomography, *in-situ* electron microscopy at high or low (cryogenic) temperature, energy dispersive X-ray spectroscopy, elemental chemical mapping. The microscope is equipped with:

- Scanning Transmission Electron Microscopy (STEM) unit with Annular Dark Field detector;
- Energy-dispersive X-ray spectrometer (EDS), fully integrated into the microscope;
- High-resolution CCD camera for image and electron diffraction recording;
- Holder with one tilting axis (single tilt);
- Analytical holder with two tilting axes (double tilt);
- Holder with two tilting axes (double tilt) for *in-situ* heating of the sample;
- Holder with two tilting axes (double tilt) for *in-situ* cooling of the sample;
- Software platform for TEM/STEM image and EDS spectra acquisition and processing;

- Tomography kit for TEM/STEM including electron tomography holder and software platform for automated TEM/STEM image acquisition at predefined tilting angles, 3D image reconstruction and visualization;
- Unit for electron diffraction with the precession of the incident beam;
- Water cooling system with closed circuit;
- UPS unit.

#### *Current state of fuel cell/electrolysis studies*

A number of papers with contributions from the laboratory on microstructural characterisation of materials for applications in energy conversion technologies have been published (Khalakhan, Lavková et al. 2017, Haydous, Scarisoreanu et al. 2018, Somacescu, Cioatera et al. 2019, Wachowski, Szpunar et al. 2020).

#### *Interest of the facility in prospective fuel cell/electrolysis studies*

The laboratory is already investigating electrodes for fuel cell applications. As a possible perspective, it is worth mentioning Identical Location (IL)-TEM to follow catalyst degradation. This can be done with the current facility, depending on the electrode allowing TEM grid insertion. The scientist in charge of HRTEM mentioned the possibility of *operando* TEM techniques, for TEM investigations in controlled gas atmosphere, in liquid environment, at varying temperatures, under electrical bias, etc. This will require substantial funding, and the laboratory is willing to write specific proposals on structural funds dedicated to such techniques, which would be extremely promising for electrocatalyst and electrode studies.

Very recently, the new 4D scanning transmission electron microscopy (STEM) nanobeam electron diffraction has been used as a very powerful tool to measure the lattice strain of individual catalyst nanoparticles with sub-picometer precision (Mukherjee, Gamler et al. 2020). Such a unique instrument would be highly beneficial to understand and engineer strain in core@shell electrocatalysts enabling to tune and enhance their catalytic activity for high fuel cell performance.

### **2.7.2. Electron Paramagnetic Resonance (LASDAM, Magurele)**

Director: Ionut Enculescu ([encu@infim.ro](mailto:encu@infim.ro))

Deputy director: Corneliu Ghica ([cghica@infim.ro](mailto:cghica@infim.ro))

#### *Description of the facility*

The EPR/ESR facility covers research fields such as physical phenomena in nanometric particles, characterisation of bulk and nanostructured semiconductor and dielectric materials with applications in nanoelectronics and nanophotonics, characterisation of materials for radiation detection and conversion, production of new catalysts, biomolecules and biomaterials investigation, creation of new medicines, understanding of living organisms functioning etc.

The facilities have the following techniques available:

- Various multifrequency and multi-resonance ESR experiments in the temperature range of 3.8 K < T < 500 K.
- Continuous wave (cw) ESR experiments in the X (9 GHz) and Q (34 GHz) microwave frequency bands.
- Fourier Transform and electron spin relaxation time measurements by Electron Spin Echo (ESE) and Free Induction Decay (FID) techniques.
- ESEEM and 2D-HYSCORE measurements.
- SECSY and EXSY measurements of the correlations and exchange rates.
- Pulse ENDOR (Electron Nuclear Double Resonance) experiments to measure the hyperfine interaction between nuclear spins and paramagnetic electrons.
- Pulse ELDOR (Electron Double Resonance) and DEER experiments to measure long-range distances by electron-electron spin dipolar coupling.

*Current state of fuel cell/electrolysis studies*

This facility is currently not active in the fields of fuel cells.

*Interest of the facility in prospective fuel cell/electrolysis studies*

The LASDAM scientists are very interested moving in the FC research field; They are partners in an ITN proposal submitted in 2020 entitled "Rational design concepts of transition metal-based ceramics toward powerful electrocatalysts for renewable energy".

In addition, a newly hired staff member has experience in the field, recently having performed his PhD at the University of Fribourg. Several examples of *operando* EPR Fuel cells are described in literature, which can serve as an example (Niemöller, Jakes et al. 2016). *Operando* EPR has for example been used to look at the degradation of the polymer membrane in PEMFCs (Panchenko, Dilger et al. 2004) or studying AEMFCs (Wierzbicki, Douglin et al. 2020).

## 2.8. Slovenia

Slovenia participates to CERIC-ERIC by sharing several NMR spectrometers hosted by the Slovenian NMR Centre in Ljubljana.

Director: Janez Plavec ([janez.plavec@ki.si](mailto:janez.plavec@ki.si))

Deputy director: Primoz Sket ([primoz.sket@ki.si](mailto:primoz.sket@ki.si))

Responsible solid-state NMR: Gregor Mali ([gregor.mali@ki.si](mailto:gregor.mali@ki.si))

### 2.8.1. Slovenian NMR Centre (Ljubljana, Slovenia)

Responsible: Janez Plavec ([janez.plavec@ki.si](mailto:janez.plavec@ki.si))

*Description of the facility*

The Slovenian NMR Centre is a national facility that offers infrastructure and expertise in the field of liquid and solid-state NMR spectroscopy to scientists and researchers in academic and industrial institutions. The NMR centre was founded by Ministry of Higher Education, Science and Technology of the Republic of Slovenia on 17th of November 1992.

The Slovenian NMR centre is open to academic researchers and researchers from industrial partners. Research program of NMR centre includes data acquisition and interpretation for those who apply NMR in their research as part of basic and applied research projects or in industry itself. The annual research program is discussed and approved by the scientific council of the NMR centre.

*Current state of fuel cell/electrolysis studies*

There is no current ongoing Fuel Cell or electro-catalytic research taking place.

*Interest of the facility in prospective fuel cell/electrolysis studies*

The facility and staff are interested, but have no experience in the field and hence do not know what might be required and or possible. There are however many *in-situ* and *operando* NMR studies on fuel cells in literature one could built upon (Blanc, Leskes et al. 2013). *In-situ* NMR focused initially on the surface electrochemistry, looking for example at the electrochemical oxidation of methanol and CO on the Pt cathode, using <sup>13</sup>C and <sup>195</sup>Pt NMR. As such reaction intermediates, products and binding to the electrodes could be characterized. To allow *operando* studies, NMR cells have been designed to integrated complete fuel cells into the NMR probe. For example, <sup>2</sup>H and <sup>13</sup>C NMR was used to study the mechanisms in direct methanol fuel cells. Another important parameter of fuel cells which can be studied using *operando* NMR is the proton transfer process (Kim, Blanc et al. 2013, Wang, Liu et al. 2016).

## 2.9. Associated instruments

### 2.9.1. X-ray Absorption Spectroscopy (Grenoble, France)

Responsible: Francesco d'Acapito ([dacapito@esrf.fr](mailto:dacapito@esrf.fr))

#### *Description of the facility*

LISA is a bending magnet beamline installed on the ESRF–EBS (Extremely Brilliant Source) ring. The bending magnet has a field of 0.85 T resulting in a critical energy of 20.6 keV. LISA consists in 3 lead hutches: the Optical Hutch (OH) containing the main optical elements, the first experimental hutch (EH1) with the instrumentation for experiments with a non-focused beam and a second experimental hutch (EH2) containing all the instrumentation for experiments with the focused beam. The monochromator allows to reach the energy ranges 4- 97 keV. The intensity is about 10<sup>10</sup>-10<sup>11</sup> ph/s.

The beamline is equipped with instrumentation for X-ray Absorption Spectroscopy i.e. ion chambers and solid-state detectors (2 High Purity Ge arrays of 12 and 13 elements, a 4 element SDD detector) a sample manipulator with 4 degrees of freedom (x, y, x and rotation). A further manipulator with 2 degrees of freedom (z and rotation) is available for grazing incidence measurements. Additional instrumentation is available for measurements in Total Electron Yield, ReflEXAFS and XEOL detection schemes. The instrumentation can be installed in either of the two experimental hutches to be used either with a large homogeneous beam (EH1) or with the focused beam (EH2). A pulsed diode laser synchronized with the storage ring Radio Frequency can be used for pump and probe experiments in stroboscopic mode.

#### *Current state of fuel cell/electrolysis studies*

LISA is involved since several year in research based on X-ray Absorption Spectroscopy on electro-chemistry, photo-electro-chemistry, fuel cells and water splitting (Wang, Lavacchi et al. 2015, Achilli, Minguzzi et al. 2016, Baran, Wojtyła et al. 2016, Miller, Lavacchi et al. 2016, Minguzzi, Naldoni et al. 2017, Berretti, Giaccherini et al. 2019). The beamline staff has collaborated with users with the aim of developing new methodologies of data collection and advanced data analysis and we are ready to start new collaborations/research programs if needed.

#### *Interest of the facility in prospective fuel cell/electrolysis studies and possible exploitation*

The hard X-ray XAS technique is a critical characterisation method used widely to study the electronic structure of materials used in fuel cells. The advantage is the probe's penetration power which is particularly handy for *in-situ* and *operando* experiments. This is because most of the catalysts used in fuel cells are high-Z transition metal materials, and therefore the L adsorption edge can be probed with X-ray beam with the energy in the range of 5-20 keV, which is sufficiently high to penetrate the liquid environment in a typical electrochemical cell.

Therefore, it is advised that this feature is further explored in the *in-situ* and *operando* studies of electrocatalysts used in the fuel cells. The instrument scientists should develop or purchase (e.g. redox.me) standard electrochemical cells which can be further tailored for their instrument. This instrument can become a CERIC's workhorse in the fuel cell research as such *in-situ* and *operando* experiments are well requested from the fuel cell and electrocatalyst research community as they are a standard for publication in high impact journals. Therefore, this instrument should stand in the forefront of the CERIC offer to this community.

### 3. New techniques/facilities proposed for CERIC tailored to fuel cell research

In this section we discuss the possible addition of characterisation techniques to the CERIC-ERIC portfolio in order to further meet the needs of the Fuel Cell community, both from academia and industry. From the industrial perspective one of the main questions is how to incorporate the new materials, which are being developed in the academic laboratories into performant devices. Such materials need to not only to work with high efficiencies and in synchronisation with the other components, but they also need to be durable and cost-effective, allowing the technology to compete with the fossil-based energy approaches. Such task is very challenging and needs advanced holistic characterisation during the operation of the device in addition to well-developed testing facilities. These would be the main drivers for the industry to exploit the CERIC-ERIC facilities. While CERIC-ERIC has several instruments that are well-tailored for the academic research in simplified electrochemical environments, it has not yet developed a systematic approach to the characterisation with the probes able to provide *operando* measurements in realistic and high-performance devices. In the following, we will discuss this point, focusing on: (i) the development of high-throughput testing facilities for industrial and academic users; (ii) use of high-energy X-ray probes; (iii) TEM methods and (iv) neutron facilities. Other important aspects are stack design and electronic control at the stack level, but these topics currently lie out of the expertise provided by CERIC-ERIC.

From the academic perspective, a few major questions and developments tackling the FC technology still remain and need to be solved: (i) development of electrocatalysts with low (or zero) PGM loading with high-performance and durability in low-temperature FCs; (ii) highly conducting and porous corrosion-resistant electrocatalyst supports; (iii) durable membranes for alkaline cells; (iv) highly conducting and durable proton exchange membranes for intermediate temperature operation; (v) nature and chemistry of triple-phase boundary; (vi) enhancing performance and durability of PEMFC for sustainable heavy-duty vehicle applications. The CERIC-ERIC consortium is well-positioned for the basic and applied research in electrocatalysis and this should be in the main focus for further development. Many instruments fitting the needs in this research field have been identified in the CERIC-ERIC portfolio, but in general basic developments of sample environments and characterisation workflows tailored for the electrocatalysis research is missing and have to be developed in the near future. On top, several state-of-the-art techniques are suggested as addition to the portfolio, focusing of fast dynamics in electrocatalysis, versatile characterisation by Raman Spectroscopy and neutron characterisation.

#### 3.1. Testing Facility for FC materials

One of the main issues hindering the progress of the PEMFC technology is an incorporation of new catalyst materials into the MEAs. This is mainly because the new catalysts are typically developed and tested in the laboratory condition, while during the deployment they have to function in the three-phase environment and at elevated temperatures. This greatly affects both

their activity and stability. Further, the complicated three-phase boundary determines diffusion for reaction reactants to the active site and also defines the removal of reaction products. So even if the catalyst has an excellent performance in liquid environment (determined by rotating disc electrode), where the diffusion is determined only by the rotation speed of the electrode, the actual performance in the actual device is often significantly different.

Therefore, to accelerate the progress in the PEMFC development, researchers must test their new materials under realistic conditions. But facilities allowing such testing are often not accessible to the



material scientists synthesizing the materials, as well as the critical knowledge to operate the testing equipment. Thus, access to such facility would be beneficial not only for the researchers, but it would also allow to develop better standard testing protocols and provide better comparison between different materials. Similar facilities exist for testing the battery materials, but no facilities of this type still seem to exist for PEMFC testing, apart from the Pro-e-Storage Laboratory at Politecnico di Milano, that will start operating in the first semester of 2022, that is academically linked with CERIC-ERIC through long-term users.

From an internal perspective, the CERIC-ERIC consortium is well-positioned to develop such a facility, as one of their partners (MFF UK, Prague) has already in-house the critical knowledge and access to the equipment. Alternatively, or in combination with this activity, CERIC-ERIC might establish a direct collaboration with Politecnico di Milano. An FC testing facility would help to bridge the fundamental research with the industrial application, a step which is chronically missing in European R&D landscape. The development of the testing and characterisation standards would be a welcome step by both academia and industry as the current DOE standards are not sufficient anymore for the next generation of materials. CERIC-ERIC FC testing facility would need to provide integrating service of MEA preparation and subsequent electrochemical characterisation, with possibility to perform BOL and EOL *ex-situ* analysis on other CERIC-ERIC instruments. For this an expertise in MEA preparation needs to be developed as this might be an important part of helping academic partners to incorporate their materials in the final composite. Such center would be able to easily extend to other kinds of fuel cells and electrolyzers for hydrogen generation and for CO<sub>2</sub> conversion.

The initial investment (both personal and instrumental) would be substantial, but it would allow to build a worldwide unique characterisation centre which would become an integral part of the material's development for the hydrogen economy. Collaboration with Politecnico di Milano might represent a cheaper, but effective alternative.

### 3.2. Pump-probe optical spectroscopy

The key issue in ORR electrocatalysis is achieving 4 proton-e<sup>-</sup> vs. 2 proton-e<sup>-</sup> transfer to activated O<sub>2</sub> bonded to the catalytic site. In fact, not only does the 4 e<sup>-</sup> pathway provide a better current efficiency, but it also avoids the generation of oxidizing hydrogen peroxide that is a primary source of MEA degradation. This reaction mechanism is critically controlled on the one hand by the details of the electronic structure, and on the other hand by the transition dynamics among electronic levels. For this reason, several catalysts with essentially the same electronic structure have been found to exhibit profoundly different activity: this is a key reason of the difficulty in rationalizing ORR activity and its stability under operating conditions. For the same reason, similar types of electronic perturbation induced by hybridizing active centres with a range of supports

have been reported to lead to widely scattered electrocatalytic performance levels. Therefore, static electronic information is often inadequate to explain electrocatalysis because also charge-transfer (CT) rates, transient confinement of the electronic density on the O<sub>2</sub>-bonding and back-donation dynamics play a key role.

It might be worth implementing the portfolio of CERIC facilities with pump-probe optical spectroscopy methods, that would allow to attack the issue of disclosing the origin of electrocatalyst activity and its dependence on ageing under ORR conditions at the molecular level through the assessment of dynamic electronic structure. Use of this technique for *in-situ* electrochemical experiments has been demonstrated in (Bozzini, Previdi et al. 2019) and application of *ex-situ* VIS pump-probe for an insightful understanding of the mechanisms of ORR electrocatalysis in the case of porphyrin-based systems has been proposed in the groundbreaking work by Zewail et al. (Yu, Baskin et al. 1999) on O<sub>2</sub> electrocatalysis by ruthenated Co-porphyrins and more recently continued (Zuo, Cheng et al. 2017) for the investigation of GO/Co-porphyrin hybrids. These two studies have unequivocally shown that differences in CT state dynamics parallel the differences in the ground-state electrocatalytic properties.

### 3.3. UV Resonance Raman

The advantages of UV Resonance Raman (UVR) spectroscopy with respect to spontaneous Raman make UVR technique a suitable method for exploring the structure of various fuel-cell materials in solid and liquid phase. The UV resonance enhancement not only leads to a significant increment of the detection limit, but also enables probing of specific parts of molecules through an accurate tunability of the excitation wavelength. Moreover, Resonance Raman with excitation wavelength lower than 250 nm allows to obtain Raman spectra of a much better quality, owing to the lack of fluorescence interference. This is particularly crucial for the case of samples at very low concentration, such as catalysts, surface species and degradation products, where excitation in the visible or near-Infrared range does not yield Raman spectra with the same signal-to-noise ratio. The full exploitation of UVR has so far been limited by the lack of tunable excitation sources of appropriate intensity that allow to finely approach the resonance conditions of specific targeted molecular groups. Additionally, the chance of extending the unique capabilities of UVR to the UV domain (i.e. up to 8 eV) opens the possibility to cover the whole range of outer electronic excitations in matter. The synchrotron-UV Resonance Raman (SR-UVR) instrument developed at BL10.2-IUVS beamline of the Elettra synchrotron radiation facility takes advantage from the wide and tunable emission in the UV range of the synchrotron source. This offers the unique opportunity to finely tune the photon energy to exactly match the electronic absorption transitions of the sample, thus enhancing the Raman signal coming from a set of chromophoric segments in the molecules. Moreover, the IUVSOffline beamline (that is among the facilities offered by CERIC-ERIC) is available for experiments with conventional UV laser sources.

Recently, particularly effort has been dedicated by the beamline staff to the development of new technological solutions for *in-situ* and *operando* UVR spectroscopy to be carried out on IUVSOffline beamline. The particular design of the sample holder and scattering geometry of Raman apparatus allows to develop integrated set-up for collecting UVR spectra in *operando* conditions. Specifically, *operando* UVR spectroscopy can be exploited for investigating the structures of fuel-cell materials at various length scales from bulk to nanoscale while they are functioning by analysing the change of vibrational fingerprints of the materials to derive the molecular structures while they are functioning. *Operando* UVR setup can be a useful tool for example for the spectroscopic characterisation of materials undergoing reaction coupled simultaneously with measurement of catalytic activity, for monitoring the time progress of chemical reactions, for following in real time the evolution of electrocatalysis and degradation chemical-physical processes with molecular selectivity. This upgrade could be particularly benefit for the studies of fuel cell, i.e. for the investigation on the performance and stability of proton exchange in membrane fuel cells or for the study of the water distribution inside the membrane or for following how electrolyte degrades as a function of cycling or for understanding how different electrolytes in a non-aqueous environment interact with the catalyst material when we do oxygen reduction. Some examples of these studies on fuel cells performed by using visible Raman or Surface-enhanced Raman spectroscopy (SERS) have been reported in literature (Li, Blinn et al. 2018). The use of UVR technique would allow to further extend the application of Raman spectroscopy to the field of fuel cells overcoming the typical limitations associated to the use of standard Raman technique (relatively low detection limit, strong interference of fluorescence background, limited selectivity of chemical groups).

In order to complete the *operando* UVR setup, the IUVS@Elettra staff is planning to couple an optical microscope (optimised for UV radiation) with the Raman spectrometer available on IUVS, for having high magnification visualisation of the sample and Raman analysis with a microscopic laser spot. This modification is expected to allow a reduction of the acquisition time for Raman measurements (thanks to the high focalisation of the laser beam on the sample) with a consequent significant improvement of the time resolution in *operando* experiments.

### 3.4. X-ray tomography X-ray Computed Micro-Tomography (XCMT)

Over the last decade, XCMT has developed into a progressively more powerful method to study PEMFCs in *operando*, in principle allowing nondestructive imaging of devices exhibiting limited modifications with respect to real-life devices and XCMT is a promising tool for the study of model devices or cells dedicated to the study of MEAs or GDEs. In fact, XCMT enables analyses of structure at scales ranging from submicron to fractions of millimeter, with lateral resolution anticorrelating with the probed volume. A potential CERIC partner based at the Elettra site, could be the synchrotron beamline SYRMEP@Elettra (coordinator: Giuliana Tromba, [giuliana.tromba@elettra.eu](mailto:giuliana.tromba@elettra.eu)) and the offline TomoLab laboratory (coordinator: Lucia Mancini, [lucia.mancini@elettra.eu](mailto:lucia.mancini@elettra.eu)). Neutron and synchrotron X-ray *in-situ* imaging can be applied as complementary tools for PEMFC studies. In these electrochemical energy storage devices, liquid water plays a crucial role in that, on the one hand, an appropriate amount of it is required for proton conductivity, but, on the other hand, flooding of gas-transport channels and porous gas diffusion layers cuts the limiting current density. Neutron and synchrotron X-ray imaging methods – initially radiography (Banerjee 2018, Kulkarni 2019) and subsequently tomography (Kulkarni 2020) - are unique methods to investigate the liquid water distribution in a fuel under realistic operating conditions. Their complementarity lies in the fact that neutrons penetrate the metallic components easily and are highly sensitive to hydrogen and can thus be employed for the imaging of entire cells, without the necessity to adapt the cell components to the imaging technique. X-ray imaging, instead, allows high spatial resolutions (ca. 1  $\mu\text{m}$ ) and fast imaging with time resolutions of some 100 ms, in the case of radiography. The drawback of X-ray methods is, however, that optical windows have to be placed in the metallic cases or end-plates, for beam access. But this can be circumnavigated by using X-rays in a high energy range (50-500 keV). In addition to water management issues, XCMT has also been employed for the study of GDE degradation (James, Choi et al. 2012, Pfrang 2013, Odaya 2015), Pt distribution (Pokhrel 2016) and structural modifications of catalyst layers and ionomer membranes (Meyer 2016, Meyer 2017, Ramani 2019) as well as the performance of innovative materials, such as metal-foam flow-fields (Fly 2019).

### 3.5. High energy X-ray characterisation

The need to study the materials in their native environment is paramount in the FC research. Given the not so well defined conditions inside the Triple Phase boundary, any information regarding the material in the running fuel cell is very helpful. Such studies would need a probe transparent Fuel Cell which would not compromise the cell performance, enabling study of the materials at elevated temperatures, pressures and controlled humidity. This can be currently achieved only by a high energy X-ray probe (50-150 keV), which provides a necessary penetration of the cell housing (Martens, Chattot et al. 2021). At such high energies the valence absorption edges are not available, therefore elastic scattering and absorption characterisation is preferred.

One of the ideal techniques are the X-ray nano/micro-computed tomography mentioned in the previous paragraph. Further, Wide and Small Angle X-ray Scattering (WAXS/SAXS) can be also employed (Martens, Vamvakeros et al. 2021). The combination of these techniques allows true *operando* experiments at the device level, revealing information about the nanoscopic processes at the materials bulk and on the interfaces. This information is instrumental both for the academic users as well as industry as it allows optimization of the materials for commercial deployment.

Given the above, it is advised that CERIC-ERIC add such characterisation to the portfolio of the instrument. However, only handful of synchrotron beamlines can provide sufficiently high energy for this kind of research, which can be a problematic point. It is advised to extend collaborations into this effect with facilities like for example MAXIV, Diamond Light Source and the ESRF.

### 3.6. Transmission electron microscopy

For the understanding of the structure-activity-stability relationship that is crucial for fuel cell and electrolysis core materials, transmission electron microscopy is an essential tool. In particular, morphology, dispersion, structural phase, and exposed crystal planes are essential in the understanding the activity of the electrocatalysts and therefore in their development and optimisation. In the frame of CERIC-ERIC, the High-Resolution Transmission Electron Microscopy at LASDAM (Magurele, Romania) is available and already involved in the investigation of electrodes for hydrogen production and conversion, reported in a consequent number of publications (see paragraph 2.7.1). Together with the electroactivity, the stability of nanocatalysts under the harsh conditions of pH, temperature and voltage they experiment in fuel cell and electrolyser is a major challenge. It is of great interest to monitor the morphological and structural modifications occurring under electrochemical operation, giving rise to a drop of activity over time. Deeper insight in the degradation mechanism depending on catalyst and support could be highlighted using *operando* TEM techniques. The latter are very challenging, allowing microscopy investigations in controlled gas atmosphere, in liquid environment, at varying temperatures, under electrical bias, etc. The introduction of such technique will require on the one hand substantial funding for the equipment and on the other hand specific skills and training of the operator. The LASDAM laboratory showed interest in writing specific proposals on structural funds dedicated to *operando* techniques, which would be extremely promising for electrocatalyst and electrode studies.

Meantime, a short-term solution, allowing to evaluate precisely the degradation of catalyst and support materials upon electrochemical cycling is the Identical Location (IL)-TEM. The monitoring of the samples would be in this case *ex-situ*. However, the identical particle location on the same grid observed before and after the stress test would allow to follow the shape and structure evolution identifying the degradation steps, observing for the same particle population, possible dissolution, reprecipitation, detachment upon support corrosion, etc... This should be possible using the current facility, the main modification would concern the used TEM grid and the electrode allowing its insertion.

Another technique which could be of interest for deep investigation of fuel cell and electrolysis materials is the 4D scanning transmission electron microscopy (4D STEM) (Ophus 2019). While in conventional STEM detectors record a single value per probe position, in 4D STEM, the probe is scanned on the specimen in a 2D array. At each probe position, a 2D diffraction pattern is imaged on a detector, generating a 4D data cube that can then be further analysed. 4D STEM allows virtual imaging producing high signal to noise ratio images, as well as orientation mapping of high relevance to rationalise catalyst activity. Furthermore, using NBED (NanoBeam Electron Diffraction), very recently, 4D STEM allowed to measure the lattice strain of individual catalyst nanoparticles with sub-picometer precision (Mukherjee, Gamler et al. 2019, Mukherjee, Gamler et al. 2020). This highly precise and local information not accessible by other characterisation methods (in conventional X-ray diffraction, XRD, the maximum resolution is in the nanometer range, on the order of the size of the catalysts themselves, which furthermore are typically not monodisperse) is crucial to understand and engineer strain in core@shell nanomaterials, which are among the best catalysts e.g. for ORR reaction.

This large set of information on structure and morphology accessible with highly specific TEM equipment would enable researchers from academia and industry to engineer catalyst activity and stability for high fuel cell and electrolysis performance. It is therefore highly suitable for the scientific community to include such techniques in the CERIC-ERIC portfolio.

### 3.7. NIPS-NORMA Instrument at BNC

The NIPS (Neutron-Induced Prompt Gamma-ray Spectroscopy) - NORMA (Neutron Optics and Radiography for Material Analysis) Instrument of the Budapest Neutron Center (BNC) combines cold-neutron imaging and PGAA, bringing together elemental analysis with imaging capabilities with typical spatial resolution of ca. 200 mm. Imaging is less specific to hydrogen, as variation is detected via grayscale changes, but

reasonably fast time dynamics can be followed. These instrument properties make it promising for FC studies. Since this instrument is not part of the CERIC-ERIC partnership, it might be worth considering to add it to the other 9 associated BNC lines.

### 3.8. Comments on the Role of Nuclear Methods in FC Studies

In FC studies, nuclear methods have indeed been employed, nevertheless, typically, their application involves a relatively small community of experts and - possibly with the exception of neutron tomography for water monitoring -, can be still regarded as a niche topic. Nevertheless, a wider use of these approaches could contribute unique information towards a more thorough understanding of both device operation and material fabrication/durability. The uniqueness of nuclear methods is their capability of providing quantitative and direct information about light elements. Moreover, nuclear techniques can be employed for *in-situ* / *operando* measurements. The presence of two CERIC-ERIC partners that are specialists in these methods (Croatia LIBI and Hungary BNC), offer the notable competitive margin of potentially enabling use of these less common analytics in conjunction and synergistically with better-known ones, such as X-ray based ones, – thanks to its multi-technique application route – and this would thus place CERIC-ERIC in a privileged position to play a key role in the expansion of the community of FC users of nuclear techniques.

The list of implemented and potential applications is diverse and includes: whole operating single FCs and stacks, electrocatalysts and full MEAs, ceramic electrodes for SOFCs and bipolar plates and their surface protection. Nuclear methods are effective tools for the characterisation of structural quantities that directly impact FC performance of the materials (lattice position of light atoms in a lattice, hydrogen in particular, concentration and dynamics). Specifically, unlike scattering X rays and electron scattering, neutron scattering from light elements (prototypically hydrogen) can be similar to that yielded by heavier elements. As a result, neutron scattering is uniquely able to directly determine hydrogen and light-atom positions and their dynamics within crystals. Moreover, owing to the significant difference in scattering cross-section between hydrogen and deuterium, isotope substitution can be employed to gain extra insight into the structure of materials and their interaction with hydrogen. Importantly for *in-situ* work, the absorption of neutrons is low in most materials: this makes it much easier to run neutron-based experiments in comparison with soft X ray- or electron-based ones. Finally, time-resolved *in-situ* methods can contribute to monitoring the functional and mechanical evolution of nanomaterials and structures, allowing to follow particles sizes and embedded surfaces. Below, we are reporting a table listing the main nuclear techniques, in conjunction with a selection of FC-relevant applications. The methods available at CERIC-ERIC partner Institutions are indicated in blue. Laboratories implementing the other methods, could be usefully enrolled in the CERIC-ERIC Partnership.

Neutron radiography and tomography (BNC)	2D/3D imaging of water/gas distribution in FCs and stacks
Neutron diffraction (ND) (BNC)	crystal structure determination (electrocatalysts, SOFC electrodes), liquid structure determination (MCFCs)
Small-angle neutron scattering (SANS) (BNC)	electrocatalysts, GDE, structure of ionomer membranes, membrane fabrication
Total neutron scattering (BNC)	local structure determination
Inelastic neutron scattering (BNC)	electrocatalysts, GDE
Quasi-elastic neutron scattering (BNC)	GDE, water/proton dynamics in ionomer
Neutron reflectivity (BNC)	hydrogen concentration profiling: thin films and ionomers
Prompt gamma activation analysis (PGAA) (BNC)	trace element determination



Ion-beam analyses (LIBI)	2D/3D profiling of hydrogen and electrocatalyst metals
Mössbauer spectroscopy	local structure determination (non-PGM catalysts)
Positron annihilation spectroscopy	structural defects in SOFC materials
Muon spin rotation	hydrogen dynamics

### 3.9. Communication and user assistance

The scenario pinpointed the present Fuel Cell Expert Group survey bears some analogies with the one that emerged from the cognate overview dedicated to Batteries, published in May 2020, though with some notable differences, related, on the one hand, with the specific importance of X-ray methods for electrocatalyst studies and, on the other hand, owing to the large potential interest of nuclear techniques for the investigation of hydrogen-rich materials.

Globally, the scientific potential of the Consortium for Fuel Cell studies from the atomic to the device scale is unique and interest from the Instruments Scientists is polarized both by the scientific scope and by the upheaval of R&D and industrial interest for green-hydrogen technologies, but coordination of interests and efforts is still limited and warrants dedicated synergy-promoting actions. In a way similar to that highlighted in the Battery report, the CERIC multi-technique facility access scheme has hardly been exploited by the Fuel Cell community, to date.

As commented in detail in Section 2 above, the large majority (87%) of the available partner Instruments implement techniques that are likely to contribute to cutting-edge information in Fuel Cell research. Notwithstanding this notable potential, only 36% have concretely performed Fuel Cell related work, but no measurement sessions, combining both directly and indirectly relevant studies, were reported to have been accessed through the CERIC scheme and, in particular, to have exploited the multi-method option. Data collection regarding publications in the field, co-authored by Partner Facilities was probably not complete and positive information was obtained only regarding the Croatian and Hungarian Partners, the latter of which reported two publications.

In analogy with the results of the previous Battery survey, the explanation of this situation is that Fuel Cell Scientists, who are also Instrument users, access the Partner Facilities typically through well-established collaborations outside the CERIC network and the contacts with new users are limited and in many cases, attempts to carry out their experiments result is unsuccessful beamtimes, owing, on the one hand, to limited knowledge of the techniques by new/potential users and, on the other hand, scarce Instrument Scientists' background on Fuel Cell related research topics.

Sometimes the Instrument Scientists' motivation to deepen aspects of Fuel Cells science and technology, that might favour access by a broader community, is limited by the fact that they see themselves as service providers for external users' groups that end up being the key players in important funded projects dealing with hydrogen technologies. Finding ways of getting the beamlines or the Consortium directly involved in large funding actions is likely to trigger and stabilize scientific interest of the Partners' Scientific staff.

#### 3.9.1. Establishment of an Access-Enabling Committee

Direct technical interaction with the multiplicity of Partner Facilities and inspection of the individual potentialities, needs and criticalities, convinced the Expert Group that a drastic increase in quality and quantity of instrument access by the Fuel Cell community would be possible if a group of experts could

act as mediators/facilitators at the interface between Instrument Scientists and potential users from academia and industry, in synergy with an enhanced communication of the analytic potentialities expressed by the Partner Facilities and compiled in Section 2. This Enabling Committee would offer concrete support regarding instrumental potentialities and limitations, as well as sample-ambient requirements, on the one hand, to potential to both users who are not converse with the methods, and, on the other hand, to Beamline/Instrument Scientists who are not Fuel Cell experts. Special care should be devoted to highlighting the potentialities of multi-technique approaches, which are highly rewarding in cutting-edge Fuel Cell studies. This is a particularly critical issue, because lack of instrument expertise by Fuel Cell experts who are not facility users, a fortiori discourages multi-method researches. From the Partners' viewpoint, the Enabling Committee can advise and concretely help the Instrument Scientists in the development of sample ambients, that can be attractive for the broader Fuel Cell community that would not be able to develop dedicated experiments independently.

In particular, the availability of this type of Enabling Committee, could favour access by potential users who are deeply involved in device issues, that are the crucially important, as well as strongly funded one, for the present and future growth of electrochemical hydrogen technologies, but that generally lack the physical background required to use CERIC facilities, but nevertheless would strongly need the kind of input that these approaches can yield, e.g. in the field of knowledge-based degradation monitoring and prediction.

It cannot be overemphasized that the Enabling Committee should be a technically operative tool for CERIC-ERIC. It is advisable to clarify this point with potential candidate members, stressing that this is not an honorary appointment, but requires concrete, hands-on involvement with Partner Facilities and users, both potential and actual, and mandates extensive and prompt availability. We recommend to avoid involving over-busy big names and rather prefer scientists who are personally and directly involved in preparing and conducting experiments at large facilities.

### 3.9.2. Institutional Scientific Communication

Enhancement of scientific communication in view of fostering Fuel Cell activities within the Consortium can be carried out along the lines suggested in the Battery report, that in our view cover exhaustively potential actions: we reproduce them with just slight modifications for the Readers' perusal. On the one hand, initial implementation of the recommendations of the Battery Expert Group show the adequacy of this approach and, on the other hand, critical review of the measures proposed therein and direct contacts with the Batter Expert Group members did not disclose criticalities or potential additions. Moreover, using a modular approach for both the Battery and Fuel Cell action with ease the implementation by CERIC-ERIC.

- (i) A webpage of CERIC dedicated to Fuel Cell work, presenting in a very light and legible way the kind of scientific information that can be achieved with the available techniques, and in particular with a multi-technique approach. Offer of help from the Enabling Committee should be advertised.
- (ii) The webpage could contain a series of virtual workshops (perhaps a YouTube channel) presenting CERIC activities in the field of Fuel Cells, and advertising synergistic use of CERIC techniques. The same platform could contain videos with few-minute (less than 4 minutes, to be lightly accessible) presentations of Fuel Cell papers describing studies, based on CERIC facilities. CERIC users can be encouraged to produce their videos right from the proposal stage. This can be done, e.g., by notifying in the proposal form their availability to produce such a video in case results from a granted beamtime are published. We believe that virtual workshops would be much more effective than de visu ones, for obvious reasons of time and costs.
- (iii) The webpage should also contain a complete and updated list of Fuel Cell papers, published under the CERIC access scheme. Of course, this option can extend to topic different from Fuel Cells, even though the existence of a dedicated "Fuel Cell library" would help. An efficient search tool for the publication database would be extremely helpful to spot specific topics.

- (iv) CERIC should endeavour to make presentations of the suite of facilities it can offer, at the main Fuel Cells/hydrogen conferences / and sessions of major electrochemistry congresses. This could go through two channels: an institutional one, i.e., CERIC people presenting the Consortium as such, and an indirect one, whereby CERIC users presenting their results could be encouraged to add a couple of slides to their talks, in which they describe/advertise the Consortium.
- (v) We have discovered that it is not easy to track CERIC-based experiments in published papers: users who have been granted CERIC beamtime should be more strongly encouraged to notify this in the Acknowledgment section of their papers. This requirement should be made mandatory by asking applicants to declare their acceptance of this condition in the proposal forms.

### 3.9.3. Funding actions

A limited amount of aimed funding could strongly foster Fuel Cell activities at CERIC partner facilities, in many cases providing the driving force to activate process that would be strongly supported by Partners, but which cannot take-off, essentially owing to lack of personnel or time. This is a condition that we have universally spotted in our survey of Partner facilities.

#### *Personnel costs*

The Expert Group is strongly convinced that the funding of thematic PhD scholarships aimed at developing Fuel Cell work at the Partner Facilities in collaboration with Academic Institutions and industrial partners, would notably help creating a network of Fuel Cell users and would enable the formation of research students who combine electrochemical and instrument skills, that is likely to consolidate in the prosecution of their scientific careers and to broaden the interest of industrial R&D laboratories towards the analytics offered by the Consortium. In addition to funding for PhDs, a few post-doc scholarships, dedicated to excellent students who completed their CERIC-funded thematic PhDs, would be effective in consolidating the cross-disciplinary topics opened up during their doctoral research.

#### *Funding for sample-ambient development*

Many Instrument Scientists complain that, on the one hand, they do not have sample ambients that could provide easy access to users from the Fuel Cell community that do not possess the skills and funds required to develop them, and, on the other hand that they do not have dedicated resources to design and build them. We believe that it would be very helpful devote some amount of funding to activities aimed at: fabricating cells, improving sample stages, implementing more adequate detectors in view of in *operando* work. CERIC might perhaps propose an internal competitive funding scheme to their Partners perhaps in collaboration with Academic Institutions, thus fostering team-building in the realm of Fuel Cell studies.

## 4. Conclusions

In this report we gave an overview of the fuel cell technology, current main research questions and reviewed the capacity of CERIC ERIC to provide a service in this field for academic and industrial users. Our global conclusion is that the available instrumental portfolio, if appropriately exploited, as such already allows to offer top-level services to FC research. Appropriate exploitation, essentially means, in synergy: (i) coordination of Partner Facilities and (ii) best use of the CERIC-ERIC multimethod access scheme. Communication will be instrumental to exploitation.

In addition to optimal exploitation of existing instruments, a strong internal research program can be developed to accelerate the development of FC technologies. Therefore we are convinced that, both in its

present setting and a fortiori after expansion of the technique portfolio, CERIC ERIC can substantially contribute to the targets set by European Commission for clean transportation and energy transition. To develop further the CERIC ERIC offerings in this field, most of the suitable instruments need to develop different type of electrochemical cells tailored for each particular technique and needs of the community. This can be done through an internal funding scheme together with several PhD projects supporting the effort. Further, the instrument staff needs to be better trained in this field and motivated to actively contribute to the academic and industrial research.

The most impact can be currently achieved by supporting the instruments in the field of electrocatalysis, where the CERIC ERIC can immediately offer a unique complementary characterisation workflows. Development of these workflows and sample environments shall be a short term priority. Special emphasis deserve neutron-based and ion-beam methods, that are currently underexploited, but exhibit tremendous potential and notable competitive margin for fuel cell work. It is recommended that the mid-term and long term priorities focus on the development of testing facilities for the device science, which is the next step necessary to help the large European research projects and emerging fuel cell industry to incorporate the newly developed materials into functional devices.

These ambitious goals will require serious organisational effort and additional funding. It is recommended that CERIC-ERIC enters the large European partnerships forming around the hydrogen economy and actively seeks funding for these activities through pillar two of Horizon Europe.

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