



## Review

# Understanding the activity transport nexus in water and CO<sub>2</sub> electrolysis: State of the art, challenges and perspectives

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## A B S T R A C T

This article reviews the challenge of expanding the current research focus on water and CO<sub>2</sub> electrolysis from catalyst-related insights towards achieving complete understanding of the activity transport nexus within full electrolysis cells. The challenge arises from the complex interaction of a multitude of phenomena taking place at different scales that span several orders of magnitude. An overview of current research on materials and components, experiments and simulations are provided. As well as obvious differences, there are similar principles and phenomena within water and CO<sub>2</sub> electrolysis technologies, which are extracted. Against this background, a perspective on required future research within the individual fields, and the need for a multidisciplinary research approach across natural, materials and engineering sciences to tackle the activity transport nexus is presented.

## 1. Introduction

Efforts are being undertaken worldwide to reduce the emission of greenhouse gases, for example, the European Green Deal and the Paris Agreement. Utilization of renewable energy is one of the most important ways of meeting emission reduction targets, which directly correlates with increased use of electrical energy, obtainable in large volumes from photovoltaics and wind turbines. While the direct use of renewable electrical energy will increase through smart approaches and electrification of industry, transport and residential sectors, the intrinsic mismatch between renewable energy supply and power demand stimulates the need for further solutions. Chemical energy conversion is seen as one of the most promising technologies that will enable us to cope with the intermittency of renewable electricity [1].

Electrical energy is used to drive chemical reactions, to either store energy in chemical bonds or produce value-added chemicals [2]. The most widely known is the hydrogen cycle, where electrical energy is used to split water in an electrolyser to obtain H<sub>2</sub> and electricity can be retrieved within a fuel cell [3,4]. Thus, two electrochemical devices are key to this sustainable hydrogen cycle. Besides the direct use of H<sub>2</sub>, a

sustainable carbon cycle can be realized through conversion of CO<sub>2</sub> with H<sub>2</sub> to hydrocarbons, while final products within a circular economy can range from e-fuels to polymers [5,6]. To implement this closed carbon cycle, classical chemical processes and new electrochemical processes, like CO<sub>2</sub> reduction, could play a prominent role [7,8]. The foundation of a sustainable carbon cycle is still sustainable H<sub>2</sub> and thus water electrolysis or direct electrochemical CO<sub>2</sub> conversion.

Electrochemical devices that can be operated at large scales will be the pillar of sustainable energy production. Electrochemical device technologies are studied in research and development, and can be differentiated by operation temperature, for example. For high temperature technology, like the solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOEC), material properties are a major challenge to commercialization [9]. In contrast, low temperature technologies, which is the focus here, have either been commercialised (alkaline water electrolysis) or are in the process of being commercialised (polymer electrolyte membrane (PEM) technology, which is in first stages of production [10–13]). Some of the intrinsic advantages of PEM technology are that it can be scaled up efficiently with high space–time yields by cell stacking and assembled in roll-to-roll processing [14]. As in most

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chemical reactors, understanding the complex interplay between the chemical reaction and transport of reactants, products and heat is crucial for efficient large-scale operation of electrochemical systems. Individual phenomena cannot be studied independently, but need to be examined within their mutual dependencies, within what we refer to as the ‘activity transport nexus’.

A major complexity for this nexus is the multiphase interactions between gases (e.g. H<sub>2</sub> and CO<sub>2</sub>), liquids (e.g. water, higher hydrocarbon products and electrolytes) and solid electrodes (e.g. carbon, electrocatalysts, and ion conducting polymer). In these multiphase systems, the mass transfer can be strongly influenced by the configurations of the porous-transport electrode (PTE). Deepening understanding of the nexus between transport and activity has allowed PEM fuel cells to achieve greatly increased efficiencies and space–time yields of devices [15]. Understanding of the transport activity nexus in low temperature water and CO<sub>2</sub> electrolyzers is less developed but is urgently needed for efficient operation.

In the past two decades, the major focus of research on both types of electrolysis applications was on developing high performing electrocatalysts to reduce kinetic losses (energy input) and increase faradaic efficiencies [16–19]. Most of this research is performed using half-cell configurations, e.g. rotating disc electrodes, with the catalyst immersed completely in electrolyte without PTE to enhance gas–liquid mass transfer and contact. However, these half-cell setups suffer from low reactant mass transport, as reflected by unrealistic current densities and potential ranges, which are significantly different from those of full electrolyser systems. Consequently, findings obtained from catalyst-structure performance relationships in half cells can only rarely be transferred to full electrolysers.

In this review article, the focus is exactly on the valley of death from innovative catalyst research towards technical electrolyser systems, which requires a fundamental understanding of the activity transport nexus under technically realistic conditions. The research on this nexus is highly complex and vibrant due to the overlay of various mass and heat transport processes, together with the electron transfer process. Methodologies and current research on the activity transport nexus within the emerging research fields of water and CO<sub>2</sub> electrolysis are reviewed which provides a perspective on how different disciplines need to come together in a joint research effort to successfully leverage the full potential of these electrochemical devices. Water and CO<sub>2</sub> electrolysis are discussed together due to their similarities. PEM fuel cells are not central to this concept paper, though parallels to this more mature technology are drawn.

## 2. Complexity of the activity transport nexus

In water and CO<sub>2</sub> electrolysers, two porous electrodes are separated by a membrane or nanoporous separator to obtain a full cell. In addition to the direct placement of the electrodes on the separator, *i.e.* the zero-gap arrangement, other cell configurations with a liquid electrolyte compartment between electrode and separator are possible [20,21]. The highly complex and interconnected main processes taking place in the electrodes need to be considered and adequately described (Fig. 1). The main phenomena are:

(i) The electrochemical reactions (both the main and the undesirable side reactions), taking place at the active parts of the electrode surface, which are influenced by the local reactant concentrations, temperature, potential and pH. The major reactions in water and CO<sub>2</sub> electrolysis are the cathodic hydrogen evolution reaction (HER) and CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR, which is a complex network of reactions) and the anodic oxygen evolution reaction (OER). For these reactions and acidic conditions and thus protons as ionic species the reaction equations are given subsequently. It needs to be noted, that for CO<sub>2</sub>RR only the simplest equation towards CO is given and that the equations need to be rewritten for alkaline conditions.

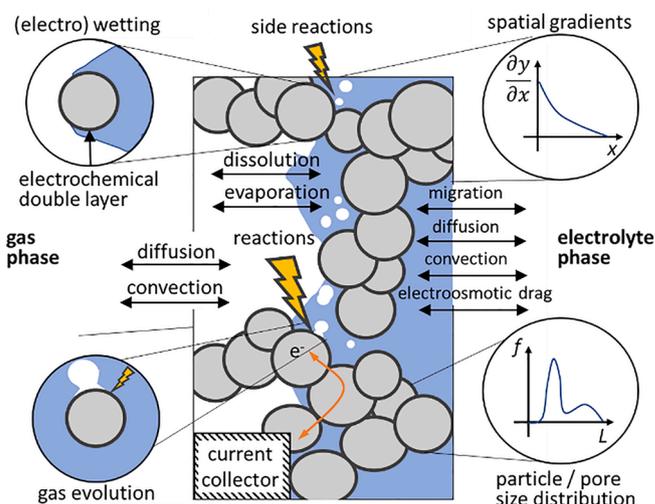


Fig. 1. Complex interaction of reaction, transport and surface processes in porous transport electrodes leads to the activity transport nexus in electrolysis.



Further non-faradaic chemical reactions may occur in electrolytes, e.g. the reaction of CO<sub>2</sub> to bicarbonate and carbonate ions [22–24]. Other undesired reactions can occur anywhere in the cell, leading to cell degradation.

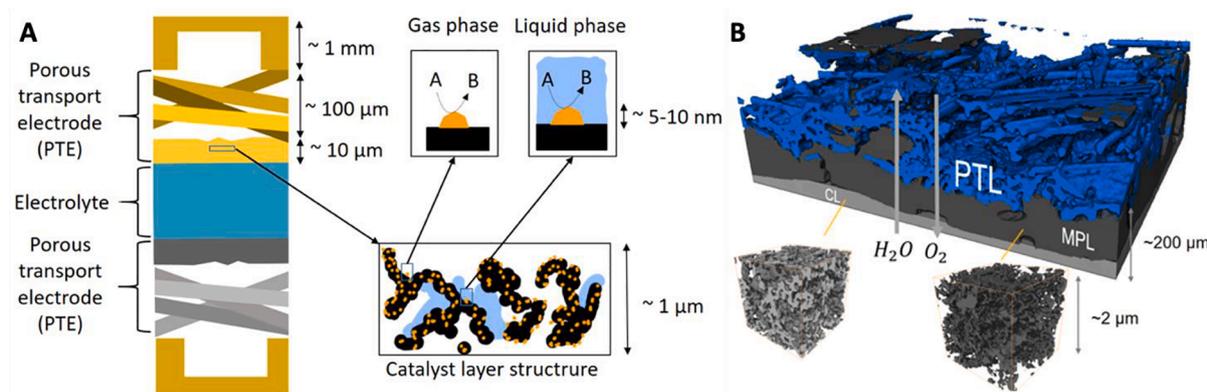
(ii) The different transport processes in the solid, liquid and gaseous phase. Whereas conduction of electrons in the electrode and of ions in the electrolyte determines the ohmic losses in the cell, mass transport limitations, especially in the liquid or solid electrolyte, frequently lead to strong gradients in concentrations and potential. Mass transport is driven by convection, diffusion, migration and electro-osmosis. Although the heats of reaction may be high, temperature gradients are often less important due to the high heat conductivity of the thin electrode and membrane layers.

(iii) The wetting of porous electrodes by reactants and electrolytes. The distribution of gas and liquid is determined by the different transport processes the hydrophilic and hydrophobic properties of the pore system in PTE, and the local pressure conditions [25–27].

(iv) The phase transition phenomena occurring in the electrodes. In water electrolysis, the products are initially formed in the liquid phase. Depending on the local mass transfer situation and the surface properties of the electrode, oversaturation and bubble formation occur [28,29]. In CO<sub>2</sub> electrolysis, the gaseous reactant must dissolve in the electrolyte before electrochemical transformation takes place and products formed can form bubbles. Thus, a three dimensional interface layer can result and in general evaporation of liquid reactants and electrolytes must be equally considered.

Additional complexity arises from the huge difference in scales (where these phenomena take place and need to be accounted) which span from the atomic level of the catalysed electron transfer, to the mm size of the microflow patterns of reactants, products, and coolants (sketched exemplarily for a membrane electrode assembly in Fig. 2a).

Given the enormous complexity of these processes taking place at the different scales of the electrodes and the entire cell, modern research on the activity transport nexus in electrolysers spans over several disciplines. Evolutionary progress in PEM fuel cell research and development in recent decades have revealed that this interdisciplinary approach can be successful. PEM fuel cells are now highly optimized systems with multiple functional electrode layers and remarkably high electrocatalyst



**Fig. 2.** a) Multiscale porous transport electrodes have decreasing size of the pores from the channel of the flow field to the catalyst layer and thus are graded hierarchical materials systems. E.g. the catalyst layers are often nanoporous materials consisting of the electrocatalysts, ionomer and binder. b) Example of a X-ray tomographic reconstruction of the porous transport layer (PTL) and FIB-SEM tomographic reconstructions of microporous layer (MPL) and catalyst layer (CL) for a fuel cell porous transport electrode, where the research field is more mature.

utilization. The main processes taking place in PEM fuel cells, including ageing mechanisms, are quite well understood. Within this review, the interdisciplinary research is structured along development of materials and components, experimental testing, and insights from simulation.

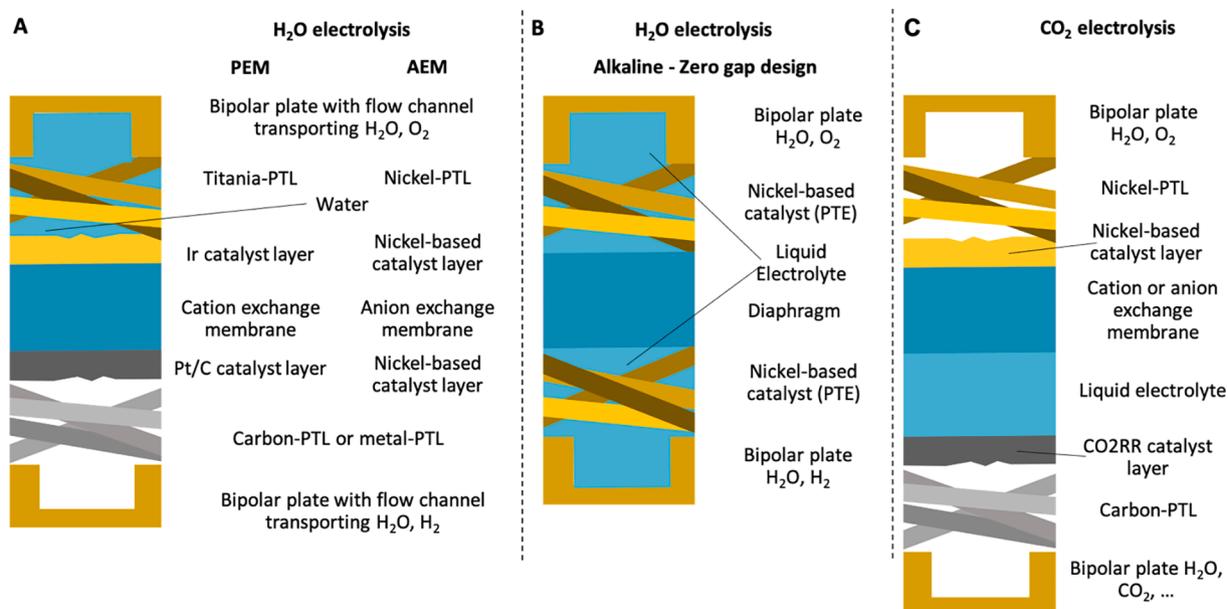
### 3. Materials and components

#### 3.1. Similarities in cell designs

A CO<sub>2</sub> and water electrolysis cell assembly typically consists of a number of different components stacked on both sides of a central electrolyte layer [30]. Fig. 3 sketches some of the most common stack designs, which shows similarities and differences in the materials and components employed. It needs to be noted, that further designs are possible and especially the anode side can differ if the OER is substituted by another reaction. The outer cell borders are made of metallic bipolar plates, as casings which work typically both as current collectors and to transport reactants in and products out of the cell. Acidic electrolysis cells usually consist of titanium, while stainless steel or nickel are preferred in alkaline ones. Moving towards the membrane, porous

transport layers (PTL) are adjacent to the bipolar plates. The PTL is also called the gas-diffusion layer, depending on the application. In this article the more general term 'porous transport layer' is used. On the anode side, structures made from titanium (acidic) or stainless steel or either nickel (alkaline) electrolyte build up the porous transport layer. On the cathode side, carbon-based structures are employed.

The porous transport layers need to enable both an electrical pathway through the solid and transport of species towards and away from the catalyst layer within the pore system. Moving further towards the membrane, the catalyst layers are the next component. Apart from a few undesirable reactions, the main reactions take place in the catalyst layers, which are a three-dimensional interface layer where electrically (solid) and ionically (liquid or solid polymer) conducting phases meet the reactant transporting phase (pores). The catalyst layers together with the porous transport layers build the porous transport electrodes. Sharp differentiation between the porous transport layer and the catalyst layer is not always possible, and the catalyst is dispersed to some extent within the porous transport layer (Fig. 2b). Finally, in the centre of the cell, a solid or liquid electrolyte layer conducts ions between the two electrodes. For water electrolysis, the separation of hydrogen and



**Fig. 3.** Exemplary structure sketches of single cells for a) water electrolysis in a PEM and AEM (anion exchange membrane) configuration, b) alkaline zero gap water electrolysis and c) CO<sub>2</sub> electrolysis with liquid electrolyte.

oxygen occurs within this component.

The electrolyte layer in acidic material systems typically consists of a solid polymer electrolyte, which is a perfluorosulfonic acid polymer with mobile protons as the ion conducting moiety and a fixed sulfonate counter ion at the polymer backbone (e.g. commercial products like Nafion™ or Aquivion®). For alkaline systems, liquid electrolytes are used as the solid polymer alternatives are either not yet stable enough or stable operation over technologically significant time scales and operation conditions has not been proven.

The catalyst is an integral part of the catalyst layer and the material used depends on the desired reaction and the pH value inside the cell. For acidic PEM water electrolysis, typical materials used are Ir-based anode catalysts for the oxygen evolution reaction and Pt-based cathode catalysts for the hydrogen evolution reaction; for alkaline water electrolysis with and without a membrane, Ni-based catalysts can be used at both electrodes. In CO<sub>2</sub> electrolysis typically with the oxygen evolution reaction, the same anode reaction and anode materials can be used as in water electrolysis. For the cathode reaction, the catalyst used depends on the product desired on the cathode side [31]. Therefore, Au or Ag-based catalysts for syngas (CO, H<sub>2</sub>) production or Cu-based catalysts for a large class of hydrocarbons, including e.g. methanol or ethene, are used. For formate production, a relatively broad range of materials, such as Sn-, In-, Pb-, Ti-, Hg-, Cd- and Bi-based catalysts, can be used.

### 3.2. Influence of materials and components on activity, selectivity, and stability

All of the components described in 3.1 influence the transport of gas and liquid reactants and products. Within the activity transport nexus, the structure and composition of these components can strongly influence the activity, selectivity, and stability of the electrolysis system. The major design criteria for the porous transport and catalyst layer are: (i) species transport with as short as possible transport pathways; (ii) countercurrent transport of mutually exclusive gas and liquid transport; and (iii) high electrode area and three-dimensional interface at active sites per unit volume of the electrode. As a result, PTEs enabling high current densities are graded hierarchical materials systems, containing large pore structures in the micrometer range for fast transport and small pores up to the single digit nanometer range in the catalyst layer.

A PTE structure of a PEM fuel cell cathode, with oxygen as reactant and water as product, is a sophisticated example of a mature materials system for this type of transport structure (Fig. 2b). Here, the porous transport electrode consists of the PTL, which is made of carbon-based fibres that are covered with PTFE to ensure hydrophobicity of the layer. The hydrophobicity allows gas transport of oxygen and gaseous water into and out of the electrode. A challenge in mass transfer is the countercurrent mode of gas and liquid transport. Another issue is that liquid water is a product in PEM fuel cells. Due to the hydrophobic PTL structure, pressure has to build up at the interface between PTL and MPL for liquid water transport to occur through the minimum fluidic resistance pathway in a burst-like process [32]. To increase electrical conductivity and to have liquid water building up between bursts, rather than blocking gas transport at the interface between catalyst layer and PTL, an additional layer was added: The microporous layer improved liquid water management and thus improved performance in the cells significantly [33]. Studies showed that predefining liquid and gas pathways in the PTL enhances the multiphase mass transfer [34] and flooding of the PTL can be prevented at high current densities. Micro-machining or regioselective manipulation of the wetting behaviour was applied to achieve these channels [35,36].

### 3.3. Current developments on porous transport electrodes/layers

The current development of PEM water electrolysis PTEs is driven by similarity to the fuel cell: Until recently, there was no interlayer between the ~ 10 µm thick anode catalyst layer of the PEM water electrolyser and

the ~ 1 mm thick porous transport electrode, with pores measuring up to a few hundred micrometers. This potentially led to damage in the catalyst layer when assembling the cells under clamping pressure, and did not ensure optimum electric conductivity to and from the catalyst layer across large pore areas of the transport electrode. Recently, a number of studies included intermediate layers in the porous transport structures between CL and PTL to create a graded transition [37]. Complemented by tomographic investigation of the interface, further development led to hierarchically structured PTLs that reproducibly showed decreased ohmic and reactant or mass transport losses [38]. These examples indicate that in PEM water electrolysis the exact form of the porous transport electrode strongly influences polarisation losses.

In CO<sub>2</sub> electrolysis, PTEs were not largely considered until recently; typically H-cell type reactors were used where CO<sub>2</sub> (dissolved in a liquid) was transported to the cathode electrode [39]. The concentration of CO<sub>2</sub> at the catalyst, however, is crucial to cell performance and the transport rate in the liquid phase can easily limit the overall device performance. There were some early studies of PTEs three decades ago, where a mixture of carbon black and PTFE (like a fuel cell MPL) was deposited onto a copper electrode, which enabled high CO<sub>2</sub> concentrations at the catalyst layer [40]. More recently, a PTE made out of pure PTFE was used together with a Cu catalyst layer and a dual carbon based additional layer, which reached current densities of up to 750 mA/cm<sup>2</sup> and faradaic efficiencies above 50% for the desired product [41]. In another study the same researchers reached current densities above 1 A/cm<sup>2</sup> with a PTE-based electrode configuration [42]. PTEs are clearly central to high performance CO<sub>2</sub> electrolysis systems and their optimum transport and optimum interface properties must be better understood. The broad range of possible products when using catalysts for hydrocarbon synthesis leads to complex interplays of liquid and gaseous products. In contrast to water electrolysis, selectivity can be largely influenced by species transport in CO<sub>2</sub> reduction. Depletion of CO<sub>2</sub> leads to lower density of adsorbed CO species and thus fewer C-C coupled products, which consequently increases unwanted HER. Despite the importance of activity and selectivity, the precise impact of the form of the interface between gas and electrolyte phase and of the PTE is not yet clearly understood. So far, this interface is defined simply by a manufacturing approach resulting in a stochastic structure.

### 3.4. Outlook

For CO<sub>2</sub> and water electrolysis, understanding of how the material structure influences multi-phase transport and how this transport couples to activity and selectivity is in its infancy. When compared to the mature field of fuel cells, the huge potential for enhancement through novel PTE structures becomes obvious. The optimum form of PTEs for a specific reaction could be reached by structured materials specifically tailored for this purpose, e.g. made of linear pores, well-defined hierarchical structures, or PTEs with predefined liquid and gas pathways. To identify new materials and components ensuring that materials in research show properties applicable for later on technical scale is very important. A portfolio spanning from well-defined model materials and components to technically applicable electrodes can minimise the materials gap between lab and technical application. Possible ways to obtain these materials could be found in 3D printing and other additive manufacturing methods, as previously demonstrated for carbon materials (Fig. 4 top) [43,44]. Ion-track etch nanotechnology could be highly attractive, as well-defined metals, metal oxides and even carbon structures can be obtained from the track etched polymer template (Fig. 4 bottom) [45]. Beside these examples new fabrication methods need to be realised for the design of novel porous transport electrodes in CO<sub>2</sub> and water electrolysis, which could then be used to deepen fundamental understanding and enhance activity and selectivity of these cells.

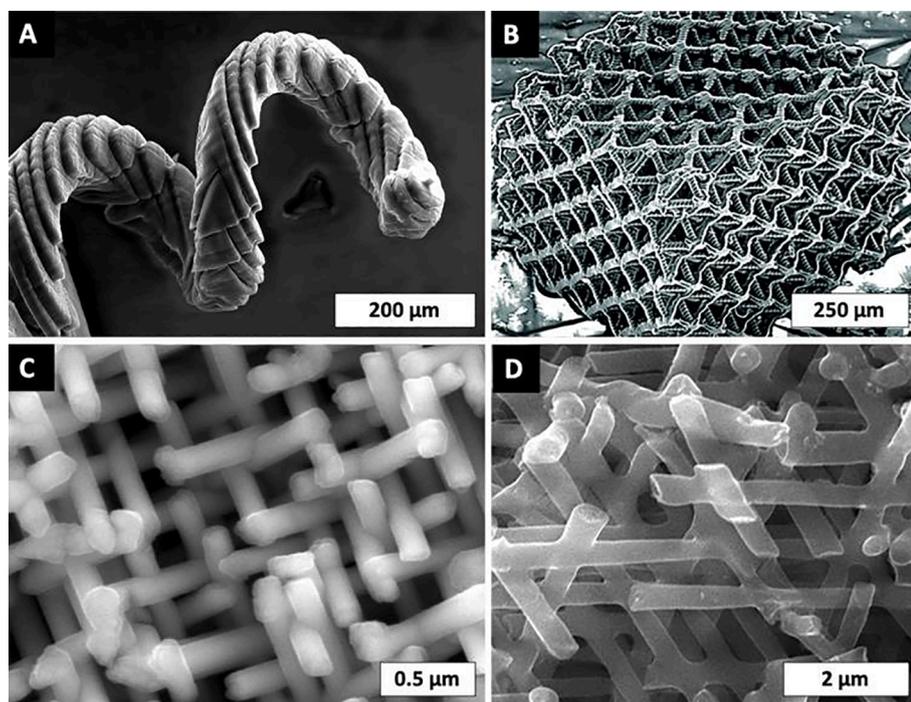


Fig. 4. a) 3D printed carbon structures derived from digital light processing printed copolymers allowing additional controllable macroporosity through porogen templating (Reprinted from [43] with permission CC BY 4.0); b) Employing a graphene oxide gel and photo resin to obtain graphene aerogels (Reprinted from [44] with permission CC BY-NC 3.0); c and d) Continuously interlinked nanostructures with controllable strut size, strut density, diameter and angle of arrangement obtained through the ion-track etch nanotechnology with CuO on TiO<sub>2</sub> (c) (Reprinted from [45] with permission CC BY 4.0) and carbon (d) (Reprinted from [46] with permission from Elsevier).

## 4. Experiments

### 4.1. Experiments with thin-film catalyst layer on a backing electrode

A central element of research on CO<sub>2</sub> and water electrolysis is investigation of the electrocatalyst. Evaluating the catalyst in a full technical cell is both time consuming and expensive and demands extensive equipment and process knowledge in engineering. There is a variety of lab electrodes and protocols available, with each having advantages and disadvantages. In these lab devices, the electrocatalyst is coated on the backing electrode to provide electrical conductivity, creating a catalyst layer which is only a few 100 nm thick. The available backing electrodes for catalyst evaluation encompass stationary electrodes, such as disks or meshes, cloths, and papers, and rotating electrodes, such as rotating disc electrodes (RDE) and rotating ring disc electrodes (RRDE). Coating is mainly done by drop casting of a particle suspension (also called ink) containing catalyst particles, an ionomer (e.g. Nafion™), and a solvent, such as 2-propanol. The ink is homogenized by ultrasonic treatment prior to drop casting. The electrode is then dried with an infrared lamp in a drying cabinet or under inert gas purging. Metal nanoparticles can be used as catalysts, either unsupported or supported on conducting substrates. This method is not limited to metal catalysts but can also be used for alloys, dichalcogenides, metal-free doped carbon materials, and immobilized molecular catalysts [47–49]. RDEs have the advantage of having a known film diffusion limitation, which allows the use of the analytical Koutecký-Levich equation to decouple film diffusion resistance in the liquid electrolyte from the remaining effective catalyst kinetics. All other phenomena, such as pore diffusion limitation within the catalyst layer, are not measured and are often not dominant, due to the very low current densities employed. RDEs are widely used in water electrolysis, with standard testing protocols proposed [50]. RRDEs allow a second electrode to be employed to electrochemically monitor liquid intermediates (e.g. H<sub>2</sub>O<sub>2</sub> and OH radicals) or products through the faradaic current of an oxidation or reduction reaction [51–53]. Stationary disk electrodes, made from glassy carbon or graphite, and carbon cloth/paper electrodes, as metal meshes, are often used in CO<sub>2</sub>RR in order to get detectable amounts of liquid products, but rarely present a PTL and enhanced multiphase mass

transfer [54–56].

The electrodes are tested in electrochemical cells typically containing a liquid electrolyte and three electrodes: the working electrode, the reference electrode, and the counter electrode. With the help of a suitable reference electrode, such as Ag/AgCl, Hg/Hg<sub>2</sub>Cl<sub>2</sub> (calomel electrode), Hg/HgO, or reversible hydrogen electrode (RHE), the electrode potential can be measured. Leak-free or low leakage reference electrodes, such as double junction reference electrodes, are used to avoid contaminations through the reference electrolyte when conventional porous junctions are used. The electrode potential can be compensated for by the ohmic resistances of the electrolyte (iR compensated potential) to get the sole faradaic resistance of the electrode, comprising the charge transfer at the electrode and possible mass transport limitations. This can be done using the current interrupt method (direct current technique) or the electrochemical impedance spectroscopy at high frequencies. Since the focus is on determining the exact current and potential of the working electrode while influences from the counter electrode and counter reaction are suppressed, these measurements are often called half-cell measurements. Catalyst screening is typically done using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements to characterize the redox behaviour of the systems and the activity of the catalyst. Measuring times are typically below 1 h. This technique is comparably cheap and very fast compared to the costly and lengthy full technical cell manufacturing and testing, which typically takes two full days plus lengthy materials preparation, such as the preparation of membrane electrode assemblies (MEA). The gas phase can be collected and analysed with the help of a gas chromatograph while the products in the liquid phase are quantified using liquid HPLC and NMR measurements or other methods.

Besides the standard 3-electrode configuration loaded with a certain amount of liquid electrolyte (“batch mode”), more sophisticated cell configurations are possible, e.g. the high-throughput cell with electrode arrays and a microelectrode tip moving over it, or the scanning flow cell (SFC), which allows a small defined amount of electrolyte to pass the electrode surface. When coupled with online analytics, the SFC can be used to investigate the product stream in the outflowing electrolyte and detect catalyst dissolution with extremely high accuracy [57,58]. The SFC has been used to boost knowledge of activity and stability of the

OER in water electrolysis [59]. Recently, this method was also extended to CO<sub>2</sub>RR, where it can be useful for activity, stability and selectivity evaluation of electrocatalysts [60].

#### 4.2. Experiments capturing the activity transport nexus

All of the approaches described in section 4.1 are based on a thin-film catalyst layer on a backing electrode tested in a liquid electrolyte. These approaches cannot capture mass transport in the flow field, the porous transport layer or the membrane of a technical cell. This has severe consequences for the activity transport nexus:

In CO<sub>2</sub> electrolysis with a cathodic PTE, CO<sub>2</sub> is not transported through the bulk liquid electrolyte as physically and chemically (depending on the pH) dissolved CO<sub>2</sub> but is supplied from the back of the PTE to a three-dimensional interface layer which is formed inside the PTE [61,62].

In PEM water electrolysis on the anodic PTE, water has to be transported from the flow field, through the PTL, to the CL and O<sub>2</sub> in the reverse direction to be released through the flow field. Hydrogen evolution takes place at the cathodic PTE, and liquid water that has been transported through the membrane by electroosmotic drag can be present. Even the mass transport losses on the cathode side can become significant [63].

In alkaline water electrolysis, the situation is simple at first glance since both electrodes are always in contact with the electrolyte and reactant water. However, similar to PEM water electrolysis [29], oversaturation of the liquid with the evolving product gases has to be taken into account [64]. The gas bubbles formed may cause a significant increase in the cell voltage due to additional ohmic resistances [65].

In PEM water and PEM CO<sub>2</sub> electrolysis, the acidic liquid electrolyte used in the half cell measurement of the electrodes is changed to a solid electrolyte: a cation exchange membrane. Thus, proton transport can change significantly and is strongly dependent on local relative humidity. In PEM electrolysis, proton transport alters with the distribution of the solid electrolyte, which depends on where exactly the CL is coated, *i.e.* on the membrane or the PTL [66], and on the coating method. Thus, specific measures, such as hot-pressing or attaching an ionomer overlayer, can help to increase the proton transport.

Mass transport limitations inside PTEs can provoke significant concentration and pH profiles, with mostly unknown conditions at the electrocatalyst. Thus, measured activities and selectivities of the same electrocatalyst can be different inside a PTE and on disk or carbon cloth/paper electrodes. This effect is particularly pronounced in CO<sub>2</sub> electrolysis using liquid electrolytes at high current densities [67].

Electrocatalysts exhibit different levels of stability in PTEs and disk or carbon cloth/paper electrodes. For example, in water electrolysis, nano- and micro-bubbles formed within the pores of the catalyst layer during the OER on disk or carbon cloth/paper electrodes cannot be removed and the corresponding potential increase can be mistakenly interpreted as catalyst degradation [68,69]. Backing electrode degradation can occur under OER conditions and has to be either excluded or considered to accurately measure the electrocatalyst's stability.

In CO<sub>2</sub> electrolysis, non-PTE electrodes suffer from a limiting current density of a few mA/cm<sup>2</sup> because the solubility of CO<sub>2</sub> in the aqueous electrolyte is limited to ~ 33 mmol/l (at 298 K and 1 atm) and the thickness of the mass-transfer boundary layer over the electrode is typically of the order of 50 μm, even when vigorously stirring or recirculating the electrolyte [67]. The limiting current density corresponds to a maximum partial current density of the CO<sub>2</sub>RR, where the local CO<sub>2</sub> concentration at the electrode drops to 0 mmol/l and the HER takes over. A possible way to push the maximum partial current density of the CO<sub>2</sub>RR to higher values is to pressurize the electrolyte, which increases the amount of dissolved CO<sub>2</sub>. For example, under 60 atm of CO<sub>2</sub> a maximum partial current density towards formate of 560 mA/cm<sup>2</sup> was reached [70]. However, the partial current densities of the CO<sub>2</sub>RR can be further increased without pressurizing the electrolyte if PTEs are used

that are in contact with gas (CO<sub>2</sub>) on one side and the electrolyte on the other, and the electrolyte can be a liquid or a solid. Partial current densities of CO<sub>2</sub>RR of more than 1 A/cm<sup>2</sup> have been reached with liquid electrolytes [42,71]. This tremendous improvement is due to two effects: Firstly, the electrochemically active surface area is greatly enhanced by optimum distribution of the gas and liquid of the three-dimensional interface layer inside the porous PTE [72]. Secondly, inside this three-dimensional interface layer the mass-transfer boundary layer is only a small liquid domain with a few tens to hundreds of nanometers of diffusion length from the gas/liquid to the liquid/solid interface [67]. Due to these two two-phase boundaries the term three-phase boundary is often used, though it is strictly speaking not correct for conventional PTEs, where the term 'three-dimensional interface layer' is more precise. The use of solid electrolytes has several advantages, such as avoiding the need to separate the liquid products from the electrolyte in CO<sub>2</sub>RR, achieving higher partial current densities, and minimizing cell voltages due to the small distances between the electrodes [73,74]. Recently, it was also suggested that a PTE could be used for alkaline water electrolysis. A properly designed pore system allowed for the transport of liquid electrolyte through the separator into the PTE, while the oxygen formed was released to the gas side. In this way, alkaline water electrolysis with only one electrolyte cycle on the cathode side becomes possible [75].

Except for the advantage of liquid product separation, all other advantages are also valid for PEM H<sub>2</sub>O electrolysis. However, the role of the ionomer gains considerable importance with solid electrolytes, since a continuous ionomer film is necessary to transport the ions towards or away from the membrane to close the electric circuit. The ionomer film controls the local concentrations at the active site (pH, CO<sub>2</sub>, products) and can be tuned accordingly.

When it comes to application-oriented measurements, full flow-cells with PTE electrodes are imperative because they are scalable in size and number (stacking). Only in this realistic arrangement can questions such as cell voltage at technically relevant current densities (typically at least 200 mA/cm<sup>2</sup>) and product crossover between the cathodic and anodic half-cell be properly addressed [20]. In the case of water electrolysis, hydrogen crossover is the main issue for safety reasons [76]. In PEM water electrolyzers, the majority of the crossover is governed by diffusion through the membrane, whereas in alkaline water electrolyzers the overall crossover is mainly determined by the mixing of the electrolyte cycles, which is necessary to keep the pH constant. Hydrogen dissolved in the electrolyte in the cathode half-cell degasses in the anode half-cell and contaminates the oxygen produced. Thus, separation of the electrolyte cycles can improve gas purity [77]. In the case of CO<sub>2</sub> electrolyzers for producing gaseous products, such as CO, or ethylene being equipped with an anion exchange membrane, bicarbonate and carbonate crossover takes place through the membrane. Because of this, the produced oxygen is contaminated through CO<sub>2</sub> release at the anode side, reducing CO<sub>2</sub> utilization [78]. CO<sub>2</sub> electrolyzers (for production of gaseous products) equipped with a cation exchange membrane and using liquid electrolytes also reveal CO<sub>2</sub> crossover due to the mixing of the electrolyte cycles, which is, similar to the alkaline water electrolysis, necessary to keep pH constant [79].

CO<sub>2</sub> electrolyzers that produce liquid products that accumulate in the electrolyte, such as formate and alcohols, can be operated in recirculating flow mode (time dependent batch operation) or continuous mode (steady state operation). In continuous mode, PFTR (plug flow tubular reactor) or CSTR (continuous stirred tank reactor) type characteristics can be realized. PFTR operation increases product concentration in the liquid electrolyte from the inlet to the outlet of the cell, whereas it keeps constant across the whole electrode during CSTR operation. Since the cathode chamber is minimized for lateral expansion, backmixing is obtained by external recycling of the electrolyte from which the product is withdrawn, and the corresponding volume is replaced with fresh electrolyte.

Flow-cell measurements are typically conducted as potentiostatic

(chronoamperometric) or galvanostatic (chronopotentiometric) measurements over long operation times of up to hundreds or even thousands of hours. Several electrochemical reaction engineering issues have to be addressed when performing flow cell experiments. First, the purity of the gases and liquids used must be carefully specified. Second, the balances must be assessed, e.g. the sum of the faradaic efficiencies or the sum of the product selectivities [80,81]. Third, the relevance of mass transport effects depending on current density must be discussed, e.g. local concentrations at the active sites and their influence on standard equilibrium potentials and product crossover through the membrane.

#### 4.3. Special diagnostics

Special diagnostic methods are very helpful to gain insight into the local reaction environment and understand the performance of electrochemical cells: the major techniques are summarized in Fig. 5. Electrochemical Impedance Spectroscopy (EIS) is often used since electrochemical workstations possess a built-in EIS. Quantitative information on resistances, such as charge transfer, ohmic losses, and diffusion resistance, or capacitances, such as the double layer capacitance, can be obtained, provided that an equivalent electrical circuit is chosen that adequately mimics the electrical behaviour of the cell. EIS has been frequently used for testing of materials, such as transition metals, p-block metals, other catalysts, and electrolytes [82]. However, few publications deal with the characterisation of PTEs, and the identification of the underlying physical and chemical processes observed in the impedance spectrum is still a matter of debate [83–85]. *In situ* IR, such as SEIRA (Surface Enhanced Infrared Absorption) and Raman spectroelectrochemistry, allows the identification of metastable surface oxides and surface intermediates [86–88] or near-electrode species [89,90].

However, these methods require thin film electrodes prepared by sputtering or chemical deposition. Fig. 6 shows that even when using a thin film Cu electrode the local pH can be increased with increasing current density due to the consumption of the protons when forming hydrocarbons and hydrogen. Differential electrochemical mass spectrometry (DEMS) is a reliable tool for real-time determination of reactant and product concentrations of a thin film deposited on a porous membrane [91,92]. Volatile products and intermediates are collected and analysed by pervaporation through the membrane.

Transport processes in multiphase flows can be investigated in operando with high time and spatial resolution using laser-optical measuring methods, without disturbing the process. These methods were mainly developed for the investigation of combustion processes [93–96].

In addition to the simple visualization of multiphase flows using Mie scattering [97,98], Schlieren imaging or shadowgraphy [99], local flow

fields can be recorded two-dimensionally [100], volumetrically [101] or in micro fluidic applications [102,103]. Very high spatial resolutions of a few micrometers and temporal resolutions down to the microsecond range are possible, even in hostile environments [104]. Temperature and concentration fields are measured pointwise, and two- and three-dimensionally (tomographic), using different linear and non-linear spectroscopic methods [105,106].

Despite their potential, optical measurement methods have only been used to a limited extent for research into electrochemical systems, such as PEM, direct methanol and solid oxide fuel cells [107–109]. The spectral range, from the UV to the mid-infrared range, opens up the possibility of measuring transport processes in single-phase or two-phase fluids in the electrolyte chamber or in the flow channels of the bipolar plate, even near surfaces. The application of these methods naturally requires an optical access. The challenge is to keep the effects of optical access on the flow and reaction properties of the cell to a minimum. Optical access can be realized, for example, by fitting the flow channels of the bipolar plate with a window. Using simple visualization with digital cameras, the formation of gas bubbles (e.g. CO<sub>2</sub>, H<sub>2</sub>, CO, and hydrocarbon species) or water droplets in the flow channels of the bipolar plate and on the surface of the porous transport layers can be observed [110–115]. These observations support mathematical modelling [116,117], for which *ex situ* investigations were also used [118–120]. *Ex situ* investigations were also used to study the transport of water through the porous transport layer by fluorescence microscopy [121,122].

An optical approach also allows the use of infrared thermography [109] to determine spatially resolved surface temperatures (of the MEA [123], for example) and to study heat transfer processes. The local current distribution can be correlated with the inhomogeneous water distribution in the cell [107] and phase change processes can be directly observed [115]. Laser spectroscopic methods have been used in electrochemical systems even less often than direct visualization and infrared thermography. These methods go beyond qualitative observation, like the simple visualization of bubbles or drops, and allow quantitative measurement of concentrations or fluid temperatures, which cannot be determined by infrared thermography. This was demonstrated in [124,125] using tuneable diode laser absorption spectroscopy. In that research, even under dynamic operating conditions, the partial pressure of water vapor and the temperature in a flow channel of the bipolar plate of a minimally modified PEM fuel cell were measured simultaneously. For higher process temperatures, like in SOFCs, a fibre-based sensor was presented [126], using ultrafast laser enhanced Rayleigh backscattering profiles for real-time temperature monitoring with reasonable spatial resolution. These pioneering works demonstrate the potential of laser optical methods.

In recent years, scattering methods, such as X-ray and neutron

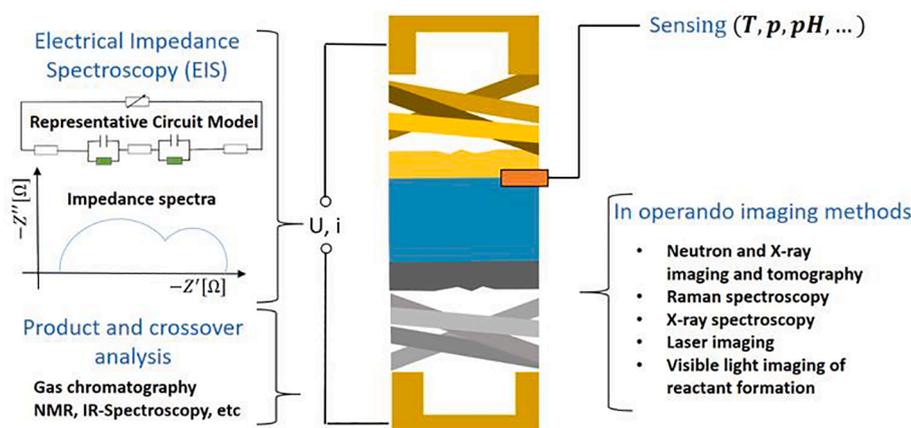


Fig. 5. Integrating characterisation methods into the electrochemical cell.

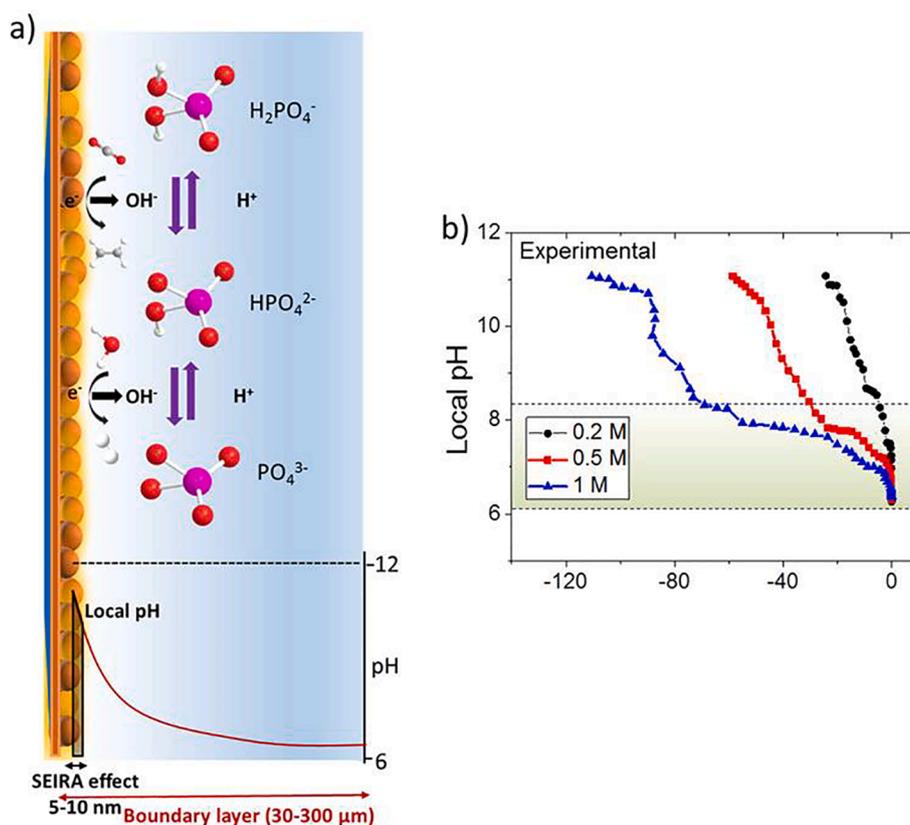


Fig. 6. Surface Enhanced IR Absorption (SEIRA) for indirect pH measurement by monitoring the local concentration of the phosphate species as a function of the phosphate buffer concentration. Reprinted from [89] with permission CC-BY-NC-ND 4.0.

scattering, have also provided important additional insight into the structural properties of porous electrodes and dynamic multi-phase phenomena in working electrolysis cells. Schuler et al. presented an in-depth study of the bulk, surface, and transport properties of PTL materials for PEM water electrolysis cells [127]. Pachenko et al. summarized earlier work on synchrotron radiography for PEM water electrolysis and presented new data on bubble formation at the catalyst layer and in the PTL [128]. Lee et al. carried out operando studies of the dynamic gas transport phenomena in a PEM electrolysis cell and demonstrated that intermittent operation may lead to an increase in gas accumulation, which negatively impacts electrolyser performance [129]. No operando radiography studies of working CO<sub>2</sub> electrolysis cells have been carried out. However, Gebhard et al. developed a special operando cell for X-ray and neutron imaging of silver-based PTE, which can be used for oxygen reduction reaction (ORR) in alkaline electrolyte and for CO<sub>2</sub>RR to carbon monoxide [130]. This cell was successfully used to monitor electrolyte transport during oxygen reduction with laboratory X-ray radiographies [131]. Increasing overpotentials results in enhanced electrolyte transport and faster droplet formation on the gas side of the PTE due to electrowetting.

#### 4.4. Outlook

In summary, there is a need for improved experimental techniques. Whereas rotating disc electrodes and H-type cells with electrodes in contact with liquid electrolyte are valuable tools for initial catalyst development, they are too far away from realistic systems, where the local reaction conditions in the porous electrodes are often drastically different from the bulk properties. Thus, cells employing PTEs are preferred [67,73]. In addition to half-cells, full cells should be employed, because only in these does the influence of the counter electrode (e.g. through crossover phenomena) become accessible [76].

Diagnostic tools, such as thin internal reference electrodes, that allow the measurement of local potentials without disturbing the electrode arrangement are especially important [132]. The use of *operando* methods to determine the local electrolyte phase distribution in working cells is highly desirable [133].

## 5. Simulation

Previous sections have demonstrated the enormous experimental efforts and challenges in understanding the activity transport nexus in CO<sub>2</sub> and H<sub>2</sub>O electrolysis. Semiempirical equivalent circuit models or Tafel equations are frequently used to identify lumped kinetic constants, apparent reaction orders, resistances, capacitances, and conductivities from electrochemical impedance measurements or polarization measurements. However, these apparent parameters lump together reaction and transport effects without providing deeper insight into the causes of performance losses or explaining the activity transport nexus. Detailed mechanistic simulations at all scales should be used to understand processes and their interactions in electrodes and cells, and to identify and quantify losses and improve electrode performance. By predicting better materials, designs and operating conditions, simulations can decrease costs and the amount of time-consuming experimental trial-and-error screening of materials and conditions.

### 5.1. Molecular and reaction kinetic modeling

At the atomic level, DFT and molecular studies allow the identification of activation, sorption and other energies as well as reaction mechanisms at typically monocrystalline electrode materials. With their study of competitive CO<sub>2</sub>RR and HER at fcc 211 stepped Pt, Norskov and colleagues presented an example of how energies from DFT can be used to parameterize a microkinetic model that in turn revealed the huge

impact of pH concentration [134]. Intensive atomistic research to identify mechanisms for the more complex CO<sub>2</sub>RR reactions at Cu is ongoing, with the main challenges being the sufficiently accurate introduction of the effects of catalyst facets, potential, and electrolyte composition [135]. Even for Cu, microkinetic models were parameterized using DFT studies. The studies thus go a step further towards bridging the gap from atomistic to microkinetic modelling, as they consider not just pH but other essential impacts as well: potential dependence and Tafel slopes or diffusion to/from the surface [136,137]. For the less complex CO<sub>2</sub>RR mechanism at Ag, such studies have even been extended to a multiscale model that contains lookup-tables from a transport model, and from DFT that feeds a microkinetic model [138]. Here, the cell transport model contains non-porous, flat electrodes but hydrodynamic layers with diffusion and migration effects at all surfaces.

There are currently only a few studies in water electrolysis that span from atomistic to mean field microkinetic models and that analyse microkinetic models [139]. A notable exception is a work from the group of Franco, whose multiscale model combines a microkinetic model for oxygen evolution derived from DFT studies with a microstructural-resolved description of charge and O<sub>2</sub> transport at the micro- and mesoscales along the anode [140]. Besides surface coverage with ionomer, the authors also evaluate different catalysts. Another recent work identified and parameterised a microkinetic model for OER on hydrous Iridium from cyclovoltammograms and showed that energies derived from the kinetic parameters match well with DFT-derived energies [141]. These works strongly contrast with other published water electrolysis models that focus almost exclusively on transport outside the catalyst layer (see below).

Significantly more effort is needed to close the gap between atomistic models of ideal surfaces, employed to obtain uncertain thermodynamic parameters, and the macrokinetic models of technical electrodes employing experimentally determined kinetic parameters. To ensure proper transfer to the macroscale, *ab-initio* parameters should be evaluated at microkinetic levels with dynamic simulations representing cyclic voltammetry, for example [142]. Purely atomistic simulations may aid catalyst pre-screening and provide parameters and pathways for microkinetic modelling, but they do not solve the activity transport nexus at porous electrodes [31,139]. No effective electrode and cell design can be done without considering transport effects and reaction-transport models [67,73].

### 5.2. Macroscopic electrode and cell modeling

Reaction-transport models at the electrode or cell level often work with a smaller set of reaction kinetic equations, but they contain a wide variety of transport effects and include geometrical or material information. They are typically based on species, charge and optionally energy balances that are discretized in at least one direction. Properly parameterized, they allow reproduction and prediction of steady state and dynamic electrochemical and concentration or surface measurements, and reveal surface states, potentials, and concentrations in and near the electrode.

Early CO<sub>2</sub>RR and HER models from 2010, with planar Au and Ag electrodes, were able to reproduce experimental partial currents and predicted a decrease in CO<sub>2</sub>RR at low potential due to accumulation of the HER product OH<sup>-</sup>, which decreases the CO<sub>2</sub> solubility [143]. Such effects are also crucial for other systems, e.g. alkaline ORR at porous Ag electrodes [144]. In 2010, Delacourt et al. integrated their CO<sub>2</sub> electrolysis model into a full cell model that included zero thickness PTEs sandwiching a liquid buffer layer and a proton exchange membrane [145]. Concentration profiles at different current densities show steep spatial changes of reactants and pH at the electrodes; the likely high impact of gas transport is also postulated. Other studies focused on cell designs with an anolyte sandwiched between two PTE [146]. Navier Stokes equations were used to model the purely liquid anolyte flow in the microchannel. Even unconventional materials, such as ionic liquids

and Bi-Sn catalysts, were considered [147]. Using a less detailed but modular and extendable model, a systematic, model-based comparison of gap and PEM cell designs for CO<sub>2</sub> electrolysis was presented by Bree et al. [148].

Models were also able to explain the experimentally observed strong performance improvement when moving from flat electrodes to partly flooded porous transport layers. In 2018, Weng et al. presented a model that compared flat vs. gas-diffusion Ag electrodes for CO<sub>2</sub>RR, and the effect of degree of flooding [72]. Whereas PTE shows better performance than flat electrodes due to their higher surface area, a complex activity transport nexus was revealed: it depends on the operating conditions whether high hydrophobicity of the electrode will improve performance.

A simplified model comparing an H-cell and a gas-diffusion layer clearly demonstrates that conditions are very different between flat and porous electrodes (Fig. 7), and that catalyst performance must be assessed under more technically relevant conditions, such as that found in porous transport electrodes [67].

### 5.3. Models with detailed gas-liquid transport and gas evolution

Models for CO<sub>2</sub>RR neglect the effect of gas evolution and two-phase flow, with most research publications being more about chemical aspects at or below the microkinetic level. Very few porous electrode or cell models exist for CO<sub>2</sub> electrolysis; for water electrolysis, the situation is the opposite. Here, except for very few studies that deal with transport effects through the ionomer [140,149,150], the focus is entirely on gas-liquid transport in electrochemically inactive layers, such as channels, membrane and porous transport layers for PEM electrolyzers [151]. The porous catalyst layer is usually not discretised and is implemented as a boundary condition rather than an object of study. Gas-liquid transport is accounted for by diffusion, convection, and Darcy's law, with saturation-dependent capillary pressure and permeabilities. Studies found the critical impact that Darcian flow has on electrode performance. Reliable parameterisation of capillary pressure and permeability is extremely difficult at present, as little data is available. This leads to uncertainties about the quantitative impact of transport on reaction [152]. More research on the catalyst layer is needed.

Many studies on water electrolysis also account for the size of formed bubbles and its effect on blockage of transport through the PTL. Whether bubbles coalesce at the channel/PTL interface or not has a strong impact on water availability at the catalyst surface, and therefore on electrode performance [150]. It can even change the Tafel slope. Besides the effect of bubbles in the PTL, bubble formation in the catalyst layer was studied as bubbles covering the surface means a decrease in electroactive area. Depending on operating conditions and bubble type, the bubbles may prematurely detach from the surface. A strong catalyst and PTL wettability is recommended to decrease bubble overpotential [28]. These studies indicate that the interaction of bubble formation/growth/release and electrochemical activity of a surface or within an electrode is highly important to quantitative understanding and prediction of gas evolving electrode performance. This even holds true for RDE level studies of oxygen evolution, where evaluation of electrochemical measurements is greatly hampered by gas bubbles. Future studies may benefit from a review of mathematical formulations of electrochemically gas evolving systems [153]. At a more macroscopic level, fluid dynamics of multi-phase flow in channels of PEM water electrolyzers are studied. They often completely disregard the activity transport nexus by assuming a constant bubble flow entering from the electrode into the channels [154,155]. Recent 3-dimensional 2-phase flow models that include the catalyst layer as an electrochemically active interfacial boundary are more helpful in resolving the interaction between transport and reaction at flow field level [156].

Besides gas-liquid transport, other transport effects such as the gas crossover effect between both electrodes warrant further attention. Up

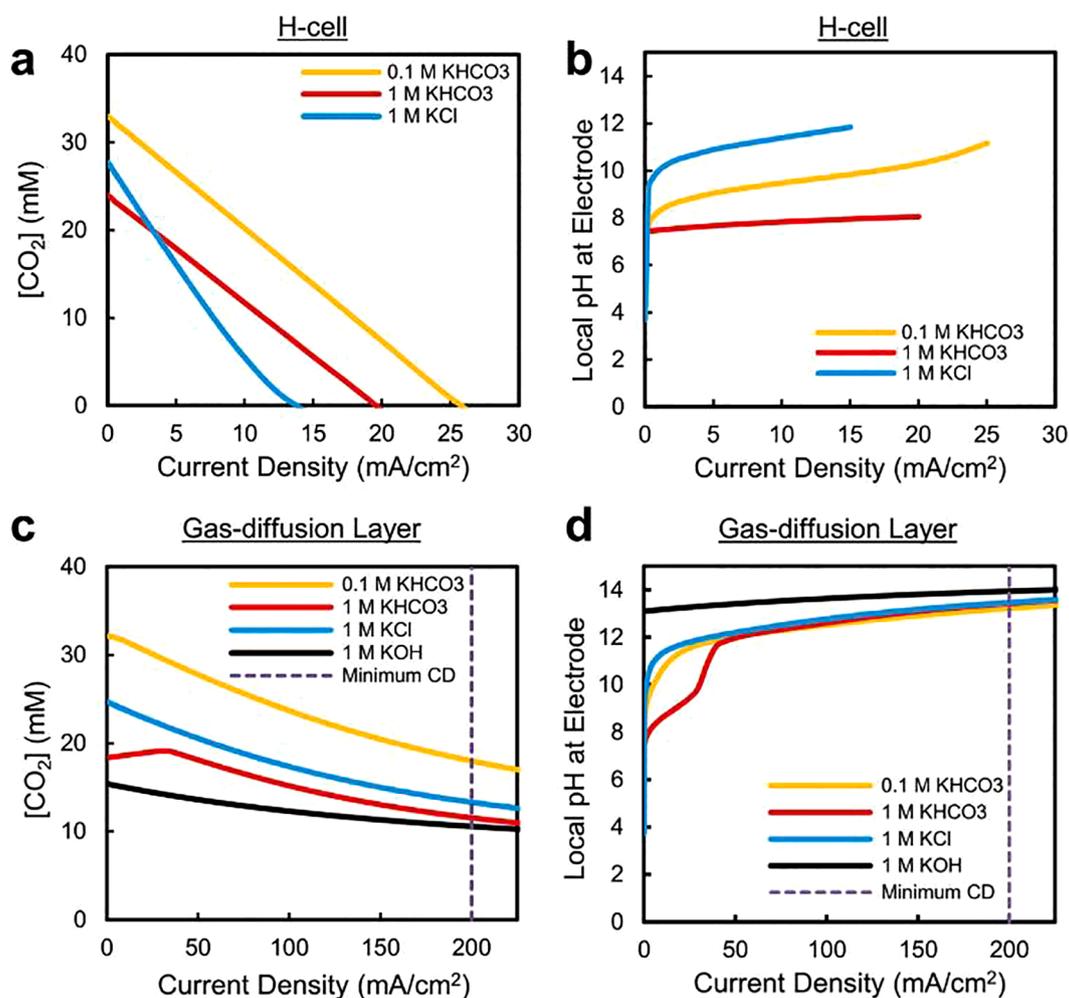


Fig. 7. Simplified model-based predictions for CO<sub>2</sub>RR of the effect of current, electrolyte and electrode design on CO<sub>2</sub> concentration and pH. Reprinted from [67] with permission CC-BY 3.0.

until now, this effect has mostly been studied for safety and efficiency. Whether crossover H<sub>2</sub> and O<sub>2</sub> is oxidised or reduced in the opposite catalyst layer, respectively, or leave the system with the other gas is known to depend on operating conditions and the catalyst-electrolyte interface [152]. However, typically it is assumed in models that the gases fully react in the opposite catalyst layer. Future modelling studies may examine the reaction transport nexus for the crossover gases at the opposite catalyst layer and at the catalyst layer where the gases evolve. An initial study analysed the effect of membrane and PTL, and postulated supersaturation in the catalyst layer [29]; the effect of properties of the catalyst layer itself have not yet been evaluated.

Whereas modelling of processes in PEM water electrolysis and its activity transport nexus lags behind PEM fuel cells, it is significantly more advanced than gas-fed PEM water electrolyzers or alkaline membrane water electrolyzers [157–159]. Alkaline electrolyzers have been around for a long time, and focus on bubble flow, bubble overpotential and current densities due to bubble influences, but with very little emphasis on the porous electrode itself [64,160–162]. The focus has been on the molecular level for CO<sub>2</sub>RR up until now, though more studies on the activity transport nexus for CO<sub>2</sub> electrolysis are expected in the future, especially regarding reaction-transport interaction and conditions in the electrode, and bubble effects or transport issues when using alkaline membranes [163].

#### 5.4. Outlook

Dynamic water and CO<sub>2</sub> electrolysis models are almost non-existent, except for more empirical system models. However, similar to fuel cells, researchers are advised to include dynamic analysis for better model validation and insight into interaction or reaction and transport processes [164,165]. As known from many electrochemical systems, there might be several mathematical solutions when identifying parameters from steady-state curves. This problem was encountered by Bree et al. in their CO<sub>2</sub> electrolysis model; they suggested model-based design of experiments for more reliable parameterization [148]. Here, dynamic analysis may be of assistance. In contrast to steady-state analysis, during dynamic operation, fast processes (such as reactions or electron transport) and slow processes (e.g. diffusion) are separated, allowing the study of their interaction and more reliable parameter identification. Standard electrochemical measurements, such as impedance spectroscopy and chronopotentiometry, build on this principle. The simple PEM water electrolysis model of Immerz et al. [166] and the cyclovoltammetry-parameterised microkinetic OER model of Geppert et al. [141] are the first steps into deeper, dynamic model-based analysis.

Also the recent trend of hybrid and data-driven models needs to be discussed. Machine learning has been mostly used to identify better catalysts after training the models on experimental data or DFT studies [167]. Machine learning might well be beneficial for models that analyse the activity transport nexus to identify or reproduce processes or

correlations. It remains to be seen how far such methods can succeed in shedding more light on the activity transport nexus.

The above analysis revealed that there is a wide range of modelling approaches for analysing CO<sub>2</sub> and H<sub>2</sub>O electrolysis, scaling from atomistic models via reaction kinetic and surface models, to fluid dynamic and cell models (Fig. 8a). Understanding the activity-transport nexus requires to couple these techniques (Fig. 8b) to analyse the interplay of processes over several scales from surface to cell level [72]. A precise description of the local conditions at the reacting electrode surface will be particularly important [168]. As model-based research on water and CO<sub>2</sub> electrolysis had different foci in the past, especially kinetic processes in CO<sub>2</sub> electrolysis (Fig. 8b) vs. 2-phase phenomena for water electrolysis (Fig. 8c), a systematic exchange of advanced models would allow to accelerate progress, and to draw general conclusions about the activity transport nexus. Finally, to reach the goal of predictive modelling of electrolysis, including model-based design of optimal electrodes, sound parameterization and close interaction of modelling, proper experiments, and profound material knowledge are needed.

## 6. Conclusion and perspectives

This review article elucidates the huge potential and challenges in new electrochemical CO<sub>2</sub> and water electrolyzers with high energy and feedstock efficiency, and optimum catalyst utilization. Given the recent progress in catalyst research it is very likely that novel catalysts for water and CO<sub>2</sub> electrolysis will be available in the future. Nevertheless, for current and future catalyst generations, full realization of the potential demonstrated needs to be achieved if these catalysts are to be employed in real electrochemical devices. Bridging this gap is key for the next generation electrolyzers, thus shifting the research focus from understanding the activity of electrocatalysts towards assessment of the activity transport nexus of electrocatalysts within full technical cells.

Any new research focus on the activity transport nexus should not draw research down to a purely technical scale. A multidisciplinary scientific approach is required and the following steps can pave the way towards realization:

- Research communities need to interact more. During definition of research questions within the fields of natural, materials, and engineering sciences, strong and vivid interaction shall be sought. When

applying these new techniques, joint research and discussion allows realization of the potential of the new techniques, towards the overarching aim of understanding the transport activity nexus.

- The possible technologies for water and CO<sub>2</sub> electrolysis have differences and similarities. Progress made in method development for, or in understanding of, a technology should be rigorously analysed and applied to all technologies.
- New and improved methods will be needed to understand the transport activity nexus. The major research fields in this perspective – materials and components, experiment, and simulation – must develop new methodologies to bridge the gap. As the coupling of phenomena at technically relevant conditions needs to be understood, there is great demand for new materials and components, experiments, and simulations. They must enable the behaviour of the systems, from lab to system scale, as well as from model systems to full technical complexity to be captured.

Based on this, future research directions in the major fields of CO<sub>2</sub> and water electrolysis can be deduced. Materials and components, with better transport pathways for combined gas, liquids, ions and electrons transport, need to be investigated and found. Contrary to the commercially available PTEs based on stochastic oriented materials, spatially optimized and hierarchically structured systems with predefined pathways - especially within the three-dimensional interface layer - are needed. To understand the contribution of materials and components to the activity transport nexus and thus the optimal pathways and structures to design, model materials of PTEs should be provided at all scales of the final hierarchy while remaining sufficiently close to the properties of real technical materials. Variation of individual parameters should also be possible to enable structure-performance relationships to be determined. Possibilities in 3D printing, nanostructuring, and spatially resolved functionalization need to be adapted and expanded to include the materials and components employed in electrolyser systems.

For experiments additional to investigations with backing electrodes bearing thin catalyst layers and aiming to determine the intrinsic catalyst properties, more and improved measurements with scalable and tailor-made PTEs should be conducted. Only with these PTEs, either in half-cell or full-cell arrangement, will the full complexity of the activity transport nexus be captured. Combining traditional stationary and dynamic electrochemical measurement protocols on PTEs with additional

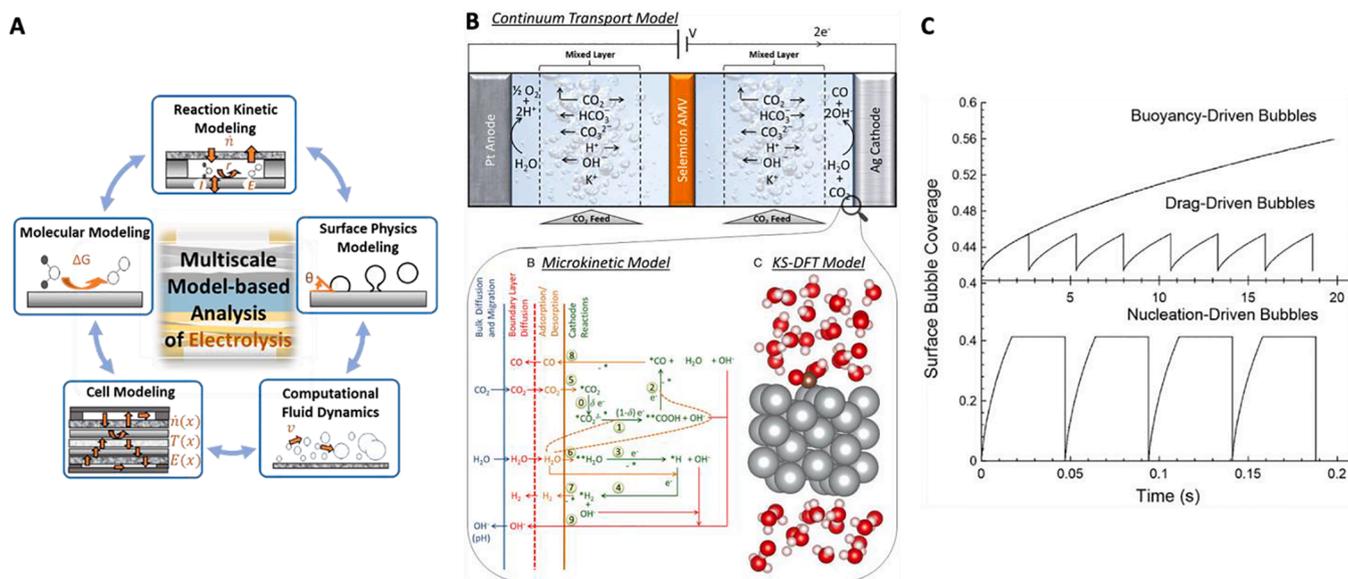


Fig. 8. a) Multiscale insight into the activity transport nexus requires exchange between or coupling of models at various scales. b) coupling from DFT to cell level model for CO<sub>2</sub> electrolysis (Reprinted from [138] with permission); c) active surface area assessed by bubble stability models in PEM Water electrolysis (Reprinted from [28], Copyright (2017), with permission from Elsevier).

operando techniques will be extremely important. Important examples are spectroscopic methods for the determination of surface species, DEMS for real-time determination of reactant concentrations, laser-optic tools for visualization of flow and phase distribution, micro- and nano-electrodes for locally resolved impedance and potential measurements, and scattering methods for the determination of reactant and electrolyte distribution in working PTEs. These improved measurements then serve as the basis for the development of better electrode and cell models.

Predictive models are an essential aid to explaining the activity transport nexus and identifying promising optimal design and operating conditions. The understanding and prediction of electrode performance needs more systematic effort to be invested in bridging molecular and macroscopic modelling via reaction kinetic and surface physics modelling, taking into account reaction, transport, and sound parameterisation. In CO<sub>2</sub> electrolysis, the strong kinetic focus of current simulations should be broadened to include transport and multiphase phenomena, and vice versa in water electrolysis.

Electrochemical technology is a very exciting future research field, comparable to the great advancements in classical heterogeneously catalysed processes that were made once the activity transport nexus was addressed in a multidisciplinary effort between natural and engineering sciences. Similar disruptive innovation could result in the development of improved electrochemical devices and processes, while the huge current interest in water and CO<sub>2</sub> electrolysis could be a fertile breeding ground for these advancements.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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