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Microfluidic tools for electrochemical energy storage and conversion: advances, applications, and research opportunities

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Electrochemical energy storage and conversion systems are essential in order to facilitate grid scale integration of renewable energy. Microfluidic systems can be a powerful tool in this respect to support and accelerate the development processes of diverse electrochemical technologies such as batteries, fuel cells, and electrolyzers. Among different applications, microfluidic systems can be considered as an analytical tool to investigate the electrochemical behaviour of various system components in real-time, gaining insight into the kinetic and mass transport losses of the system. Moreover, microfluidic cells can serve as testing platforms for screening new materials and evaluating test conditions, leading to the discovery of alternative catalyst materials and the identification of optimal design and test conditions. Microfluidic devices can also aid the synthesis of complex structures and nanomaterials that can be used as electrocatalysts in electrochemical systems. Therefore, adopting microfluidic tools for the development and optimization of electrochemical energy storage and conversion systems can accelerate the innovation process, enhance energy conversion efficiencies, and optimize the utilization of materials and resources. Overall, microfluidic cells pave the way for the next generation of electrochemical energy storage and conversion systems by providing a versatile, cost-effective, and rapid platform for fundamental studies and device optimization. This review compiles key advancements in microfluidic technology that offer valuable insights into system design and operation, accelerating development and guiding scale-up for more efficient and sustainable electrochemical devices.

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Introduction

The growing global energy demand is shaping the transition towards renewable energy sources. This shift is not only driven by environmental issues associated with the combustion of fossil fuels but is also influenced by the international sustainable development goals set by the United Nations. As nations continue to combat climate change and decarbonize, reducing their carbon emissions towards net zero by 2050,[1] the integration of renewable energy sources such as solar and wind has gained more attention and dramatically increasing investments.[2,3] Although both solar and wind are clean, renewable, and abundant forms of energy, they can fluctuate throughout the year due to weather conditions and time of day, creating the need to store the surplus energy in readily dispatchable forms, preferably using scalable methods that are amenable to distribution and bulk, long-distance transport. Electrochemical energy storage and conversion systems play a crucial role in mitigating these challenges. These systems are essential to guarantee that the energy supply and demand are met by allowing the storage of surplus energy generated during peak production times, and its subsequent release during periods of high demand, ensuring a consistent energy supply that supports both residential and industrial needs.

Electrochemical energy storage and conversion systems can store and convert chemical energy to electrical energy through redox reactions. Those systems can be divided into two groups: galvanic and electrolytic cells. Galvanic cells can convert chemical energy into electricity through spontaneous redox reactions (*e.g.*, batteries, fuel cells), while electrolytic cells need electrical energy to drive non-spontaneous redox reactions (*e.g.*, redox flow batteries, water electrolysis). A rich variety of electrochemical cell devices have been developed for a wide range of technologies such as batteries, capacitors, fuel cells, electrolyzers, solar cells, water treatment, and others. Common applications include portable electronics,[4] electric vehicles,[5] grid stabilization efforts,[6] hydrogen production,[7] and stationary power systems.[8]

Despite their many advantages, electrochemical energy storage and conversion technologies also struggle with technical limitations and the need for performance improvements. The main challenges include low energy density, limited cycle life, and cost-effectiveness.[9] While battery systems still struggle with limited lifespan, low efficiency, and high production costs,[10,11] fuel cells and electrolyzers face problems with low durability[12] and high materials and component costs, such as precious metal catalysts.[13,14] Addressing these limitations is crucial to make these systems more cost-effective and, therefore, increase the widespread adoption of clean and renewable energy systems, leading to the advancement of a sustainable society.

For further advancement of materials, devices, and technologies for electrochemical energy conversion and storage, microfluidic cells are emerging as potential analytical tools and testing platforms for electrochemical system applications, offering a cost-effective and convenient laboratory-scale approach for research and development.[15–19] Controlled environments can be achieved by enabling the manipulation of fluids and mass transport at the microscale, which is crucial for conducting detailed analyses and assessments of electrochemical interfaces. This ability to fine-tune various parameters makes microfluidic cells especially well-suited for investigating complex electrochemical phenomena in systems such as batteries, fuel cells, electrolyzers and others.

There are numerous research opportunities and applications where electrochemical energy conversion and storage systems can benefit from microfluidics. One key application is the use of microfluidic cells as analytical tools to study electrochemical reactions and elucidate complex mechanisms such as kinetics and mass transport, which can affect the overall performance of systems and can be tackled by means of refined experimental control. Thus, understanding those mechanisms is crucial for identifying limiting factors and designing improved materials and solutions, which can lead to optimal cell designs and more robust and durable devices.[20,21] Additionally, microfluidic systems can facilitate the screening and fabrication of catalyst materials, which can reduce assessment time and increase catalyst production.[22] Moreover, microfluidic systems can be useful for the evaluation of new cell designs and cell conditions that can address mass transport limitations, improve fuel utilization, enhance reaction efficiencies, and minimize losses, thus contributing to the development of more performant energy solutions.[23–25]

Various review articles have been published in the literature aiming to evaluate and demonstrate the use of microfluidic devices in different fields and applications, such as cell culture,[26] drug research,[27] chemical analysis,[28] water quality monitoring,[29] food engineering,[30] and others. For electrochemical energy storage systems, a few review articles have also been presented to date,[31–33] with a general scope on microfluidic cell designs and performance optimization, but little or no focus has been given for the application of microfluidic devices as analytical tools for the advancement of energy storage and conversion systems, even though it could open new research perspectives and opportunities with broader utility.

The present review article therefore aims to provide a comprehensive examination of the potential of adopting microfluidic cells as analytical tools for the development of electrochemical energy storage and conversion systems. In this work, we provide a summary of the recent advances and examine research potential where energy storage systems can benefit from the use of microfluidic cells. The impact that microfluidic technology can have on the development of next-generation energy storage and conversion solutions is also discussed, showing a few key applications on materials and components assessment, screening, synthesis, design, and optimization. Throughout the review, our goal is to elucidate how microfluidic systems can become an important analytical tool that can lead to a deeper understanding of the complex electrochemical processes and interfacial phenomena in these systems and also contribute to the achievement and adoption of more sustainable and efficient energy systems, shaping a cleaner energy future.

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Fundamentals

Microfluidics

Microfluidic systems. Microfluidics is a multidisciplinary field that focuses on the manipulation and control of fluids at the microscale, usually within channels smaller than a millimetre in diameter.[34] This technology has emerged as a significant advancement in analytical chemistry,[35] biochemistry,[36] and biomedical engineering.[37] It facilitates the development of miniaturized devices known as microfluidic chips or lab-on-a-chip systems. These devices can be applied in a wide range of chemical and biological analyses with high precision and efficiency.

The fundamental principles of microfluidics are based on the behaviour of fluids in small channels, where effects such as surface tension, capillary action, and laminar flow dominate over inertial forces and turbulence.[38] At the microscale, the influence of viscous forces increases, leading to laminar flow conditions where fluid layers can move in parallel without mixing. This characteristic allows for precise control of fluid motion and associated mass transport, enabling the creation of controlled environments for reactions and analyses that are important for microfluidic cells for energy storage and conversion applications. Various physical and electrochemical principles, including mass transport (diffusion, migration, and convection) and reaction kinetics, govern the interactions of fluids within microchannels. These principles are important for the design and optimization of microfluidic devices for prospective use as analytical tools.

Advantages of microfluidic systems. The adoption of microfluidic systems has been gaining more attention due to intrinsic advantages related to the micro-scale nature. One of the most important advantages of microfluidic systems is the flexible design and prototyping of experimental devices with small features, which can be modified based on the application needs, with varying channel geometries, flow pathways, substrate materials, electrode configurations, *etc.* Another important advantage of microfluidics for energy storage systems is that microfluidic cells can be designed and operated without a membrane, which not only eliminates the use of an extra component and reduces operational cost, but also eliminates the problems associated with crossover, membrane degradation and contamination, and, in some cases, water management. By eliminating the membrane, these microfluidic cells enable direct focus on electrode and electrolyte evaluation, allowing distinct observation of transport mechanisms specific to these components. This advantage is central to the membraneless microfluidic cell configurations discussed later in this review.

Reduction in sample volumes is also another advantage from the micro-scale design when compared to traditional methods, which can efficiently reduce the consumption of reagents and mitigate waste creation. Thus, the ability of microfluidic devices to run experiments with volumes of microliters is very useful in scenarios where sample availability is expensive or scarce, such as clinical studies[39] or biomedical diagnostics.[40] In addition to material operational costs, small sample volumes also reduce materials waste, which helps create more environmentally friendly laboratory assessment procedures. Additionally, reducing sample sizes makes it possible to evaluate rare or costly materials, which can be very useful in applications such as fuel cells and electrolyzers, where noble metal catalyst materials are widely adopted.[41] This makes it possible for researchers to experimentally test valuable materials in reduced quantities, eliminating the need for more resource-intensive samples to evaluate and screen catalyst materials based on their performance and properties.

Another desirable advantage is the capability of controlling and tuning microfluidic cell environment and reaction conditions, which can be crucial for understanding electrochemical kinetics and mass transport loss mechanisms. Small microchannels enable rapid activation and reaction kinetics, which enhances reaction efficiency and speeds up analysis. Researchers can tune experimental conditions within the microfluidic cell, such as reactant composition and concentration, flow rate, mass transfer rate, temperature, relative humidity, and pH, and analyze in real-time the observed changes in system performance caused by the variable manipulation to establish performance sensitivity. In this context, understanding the impact of test conditions on the electrode and cell performance is essential for maximizing the performance and durability of flow batteries, fuel cells, and electrolyzers. This advantage is particularly valuable in applications where microenvironments with specific chemical and physical characteristics are needed, such as drug screening,[42] cell cultivation,[43] and protein biophysics.[44] For electrochemical systems, the use of microfluidic systems with a controlled environment is beneficial for the synthesis of catalyst nanomaterials, where catalyst size and morphology can be tuned by strategic adjustments in reaction conditions.[45]

One of the unique advantages of microfluidic cells is their ability to be scaled down and offer a great design flexibility, enabling controlled experiments across multiple length scales relevant to electrochemical energy conversion systems. These systems involve processes ranging from the nanometer scale (*e.g.*, electrocatalytic reactions) to the meter scale in grid-level storage, with microfluidics providing a powerful bridge for nanoscale and microscale investigations. At the nanometer level, microfluidic cells serve as versatile platforms for catalyst screening, investigating complex catalytic processes, and identifying side reactions by precisely tuning operating conditions, such as flow patterns, chemical gradients, and electrolyte composition, which has a direct influence on electrocatalyst performance. At the microscale, microfluidic cells provide valuable insights into charge transfer kinetics, ion diffusion, and other transport phenomena. The knowledge gained from these controlled studies can in many cases be translated to scaled-up systems, for example, in understanding how flow rate, electrolyte concentration, and temperature impact overall electrochemical performance.

Real-time monitoring and instantaneous feedback of electrochemical performance are also possible by the

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integration of microfluidic devices with other techniques which can offer a broader, multifaceted analysis when combining electrochemical tools with physico-chemical, imaging, and spectroscopy characterization tools. This is crucial for applications where monitoring variations in system conditions can provide important information on system performance loss and degradation. Real-time monitoring and data extraction for performance evaluation and feedback enables performance improvement strategies based on sensitivity analysis. Furthermore, *in situ* and *in operando* evaluations can be done by combining microfluidics with additional optical imaging techniques. Thus, side reactions such as gas evolution can be detected, quantified, and mitigated, thereby increasing the utility for battery and fuel cell applications where side reactions can reduce system performance and lifespan.[46,47]

Challenges of microfluidic cells. Although microfluidic cells offer many advantages for studying electrochemical energy systems, several challenges must be considered, particularly when translating insights to larger-scale applications. A key limitation is that microfluidic devices may not capture spatial heterogeneities that are more pronounced in scaled-up systems, such as uneven reactant distribution,[48,49] local variations in electrode activity,[50] and large-scale electrolyte and temperature gradients.[51] Phenomena like reactant starvation,[52] hot spots,[53] uneven reaction rates,[54] and non-uniform electrode properties (*e.g.*, localized hydrophobicity)[55] can significantly affect performance in practical systems but may be absent or minimized in the controlled environment of microfluidic cells. Flow behavior also differs, with laminar flow dominating in microfluidic channels, whereas large systems often exhibit turbulent regimes that introduce additional transport complexities. Furthermore, the simplified designs used in many microfluidic studies, especially in membraneless configurations, eliminate components like separators or membranes that, in large systems, affect important phenomena such as mixing, crossover, and membrane degradation. While these differences can limit direct scalability, the mechanistic insights gained from microfluidic studies remain valuable, not only for informing aspects of large-scale system design but also for optimizing other small-scale devices, such as microfluidic fuel cells and batteries.

Microfluidic cell types. Microfluidic cell designs can be divided into two groups: **continuous flow** or **segmented flow** (Fig. 1). Each type of cell offers distinct advantages, either for electrochemical assessment or nanomaterials fabrication, which will be further discussed. While continuous flow cells are mainly used due to controlled experimental conditions, making them suitable for detailed electrochemical studies, segmented flow devices offer high-throughput capabilities for the synthesis of nanomaterials, reducing fabrication time and increasing catalyst yield production. Thus, choosing which system can be applied for specific applications depends on its nature and the research goals of the experiments to be conducted.

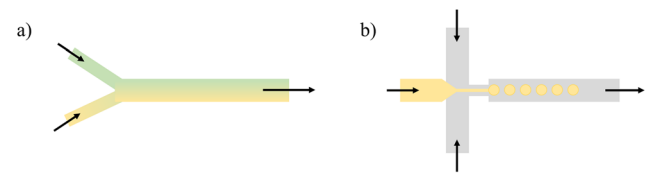

Fig. 1 Schematic of microfluidic cell types with a) continuous flow and b) segmented flow.

Continuous flow cells. Continuous flow cells are usually known for their smooth fluid flow. In the case of microfluidic cells, their small dimensions imply that viscous forces outweigh inertial forces, which ensures predictable laminar flow governed by Reynolds number (Re) below 2000. Typically, microfluidic cells operate in the Stokes flow regime ($Re < 1$), also known as creeping flow. The Peclet number, representing the ratio of convective to diffusive mass transport, is typically maintained much greater than one in order to control diffusive mixing.[32] Laminar flow cells generally consist of flow channels that are fabricated using materials such as polydimethylsiloxane (PDMS). Electrodes are placed at the base of the cell or along the channel walls, depending on the cell design and electrode configuration. By continuously flowing the reactants across the electrode surface, the electrochemical performance can be evaluated in a systematic and quantitative approach.

The main advantage of laminar flow over droplet systems is the ability to generate a steady reactant gradient with reduced convective mixing. This advantage is crucial in reaction kinetics, mass transport, and charge transfer evaluation. Laminar flow cells are widely applied in experiments using electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy, and chronoamperometry. The main applications are electrochemical reaction assessment, catalytic reaction study, and novel electrode material screening, among others.

Segmented flow cells. Segmented flow microfluidic systems offer an alternative approach for nanomaterial fabrication by encapsulating reagents within small droplets that travel through a carrier fluid that is typically an oil. In such systems, droplets act as independent microreactors and environmental conditions can be tuned for desirable outputs. By tuning synthesis conditions, researchers can perform investigations on their impact on catalyst size and morphology. Additionally, segmented flow systems create opportunities for the synthesis of complex structures which cannot be synthesized using traditional methods. Thus, these systems enable innovative approaches to produce catalyst materials in a faster and more efficient way, broadening the application of catalyst materials in electrochemical energy storage devices.

Electrochemistry

Cell potential. Electrochemical cells are devices that convert chemical energy into electrical energy, or *vice versa*, through electrochemical reactions occurring at electrode–electrolyte interfaces. A typical electrochemical cell consists

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of two electrodes (electronic conductors), an electrolyte (ionic conductor), and an external load circuit as main components. The system can be divided into two half-cells, where both oxidation (reactants losing electrons) and reduction (reactants gaining electrons) reactions occur (eqn (1) and (2)), and electrons are transferred between chemical species at the anode (electrode where oxidation occurs) and cathode (electrode where reduction occur). Those reactions can be written as:

$$\text{Negative half-cell: } A^{m+} \rightleftarrows A^{m+} + xe^- \quad (1)$$

$$\text{Positive half-cell: } B^{n+} + xe^- \rightleftarrows B^{(n-x)+} \quad (2)$$

The cell potential (E) is the difference of the cathode and anode electrode potentials, and indicates the driving force and spontaneity of the redox processes. The Nernst equation is used to predict the cell potential based on the two half-cell reactions and their operating conditions (eqn (3)). The Nernst equation can be expressed as:

$$E = E^0 - \frac{RT}{nF} \times \ln\left[\frac{\prod a_{\text{Products}}^{\nu_i}}{\prod a_{\text{Reactants}}^{\nu_i}}\right] \quad (3)$$

where E^0 is the standard cell potential, R is the universal gas constant, T is the cell temperature, n is the number of electrons involved in the reaction, and F is Faraday's constant. In the equation, a refers to the activity of each species and ν_i refers to its corresponding stoichiometric coefficient.

The interfacial interactions at the electrode–electrolyte interface impact the charge transfer processes and kinetics of the electrode reactions. Thus, different losses can result from interfacial phenomena. For that, we account for overpotentials (η), which is the difference between the theoretical reversible potential and the actual potential required to drive a reaction. The main overpotentials of an electrochemical cell (Fig. 2) are attributed to open circuit voltage (OCV), activation, concentration, and ohmic losses within the cell, where both anode and cathode electrodes contribute to activation and concentration losses while the electrolyte is the main contributor of ohmic loss. The sum of the various overpotential contributions can be expressed mathematically as:

$$\eta = \eta_x + \eta_{\text{act}} + \eta_{\text{ohm}} + \eta_{\text{conc}} \quad (4)$$

where η_x represents OCV overpotential caused by parasitic losses (crossover, shorts, impurities, *etc.*), η_{act} represents activation overpotential related to the energy barrier for the reaction to occur, η_{ohm} is the ohmic overpotential that is related to the resistive losses in the electrolyte and electrodes, and η_{conc} is the concentration overpotential related to concentration gradients of reactants and products near the electrode surfaces.

Kinetics. Understanding the kinetics of reactions and associated activation overpotential mechanisms in electrochemical systems is crucial for enhancing device performance and efficiency. The kinetic analysis examines the rates of electrochemical reactions, their reaction mechanisms, and how various factors—such as the reactant concentration, temperature, and physical and chemical properties of electrode surfaces—affect them. Kinetics play a vital role in the overall efficiency of electrochemical cells, as the rate of electron transfer at the electrode–electrolyte interface is reliant on the rate of these reactions. The impacts of mass transport limitations and charge transfer resistance must also be explored, as they significantly affect kinetic rates.

The Tafel and Butler–Volmer equations frequently appear in literature for electrode kinetics evaluation. The Butler–Volmer equation (eqn (5)) is derived from the relationship between activation overpotential and current density:

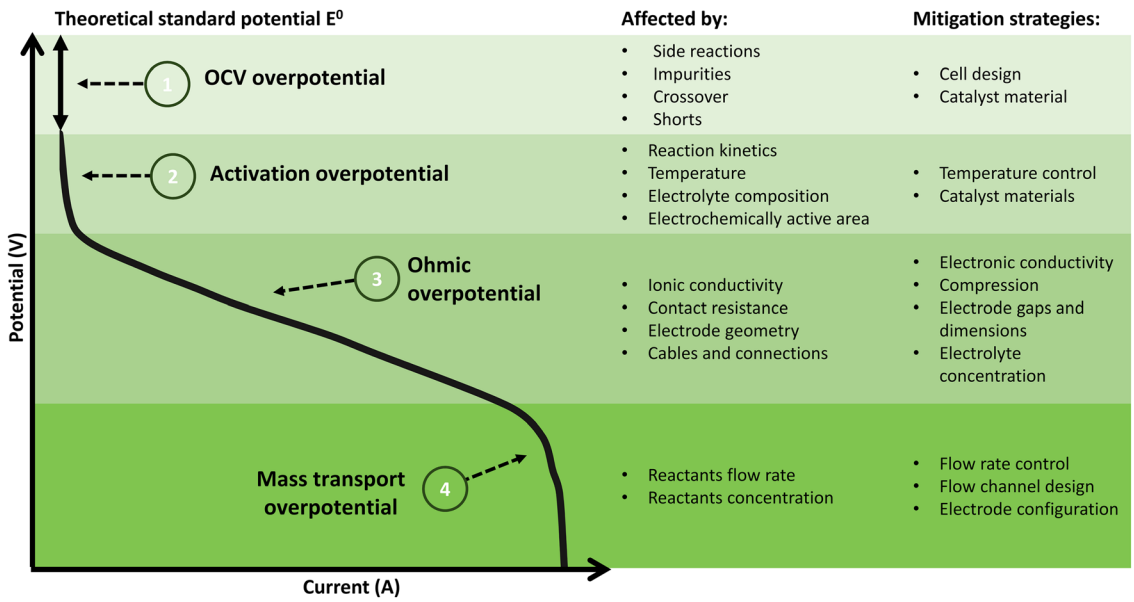

Fig. 2 Cell polarization curve with detailed overpotentials and mitigation strategies.

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$$j = j_0 \left[\frac{c^{s}_{\text{Reactants}}}{c^{b}_{\text{Reactants}}} e^{\left(\frac{\alpha n F \eta_{act}}{RT}\right)} - \frac{c^{s}_{\text{Product}}}{c^{b}_{\text{Product}}} e^{\left(\frac{-(1-\alpha) n F \eta_{act}}{RT}\right)} \right] \quad (5)$$

where j represents the reaction current density, j_0 is the exchange current density, α is the charge transfer coefficient, c^{s} represents the species concentration at the electrode surface, and c^{b} refers to the corresponding concentration in the bulk solution (for both products and reactants). When studying electrode kinetics, it is important to consider any concentration gradients and maintain constant surface and bulk concentrations. One method to accomplish this is by mixing the solution to minimize mass transfer limitations, such that the rate of mass transport exceeds the rate of reaction, which allows for the simplified version of the Butler-Volmer equation given by eqn (6). Alternatively, microfluidic systems can reduce mass transfer limitations and control the rate of reactant supply by utilizing microchannels.

$$j = j_0 \left[e^{\left(\frac{\alpha n F \eta_{act}}{RT}\right)} - e^{\left(\frac{-(1-\alpha) n F \eta_{act}}{RT}\right)} \right] \quad (6)$$

Microfluidic cells can be a powerful analytical tool for kinetic assessment due to their precise control over reaction environments and the ability to tune key test parameters that influence kinetic reactions. The small dimensions of microfluidic channels enhance mass transport and reduce diffusion paths, allowing faster response times. Thus, fast electrochemical reactions can be analyzed, which might be difficult to study in traditional characterization tools and setups such as static three-electrode cells. Useful insights can be extracted from microfluidic cell kinetic data, which can improve battery performance and catalyst efficiency, as well as electrode design. In literature, Tafel curves have been plotted, and kinetic parameters were studied for both electrode materials and different redox chemistries to understand sluggish and limiting performance factors.

Mass transport. Another important factor that can impact system performance is mass transport. Mass transport mechanisms in electrochemical cells involve the movement of reactants from the bulk supply to the electrode surface and the removal of products away from the surface. Ensuring efficient mass transport is crucial for maintaining the optimal concentration of reactants and products so that the electrochemical reactions can proceed at high rates and with low overpotentials. Limitations in mass transport, such as reactant supply, single-phase diffusion, and, in some systems, liquid water flooding or gas bubble accumulation, can lead to concentration gradients, higher overpotentials, and reduced overall system performance. The three main transport mechanisms in electrochemical cells are **diffusion**, **migration**, and **convection**.

Diffusion is defined as the spontaneous movement of reactants and is driven by the concentration gradient of species. Fick's first law of diffusion states that the flux (J) of a species is proportional to the concentration gradient (∇_c):

$$J = -D\nabla_c \quad (7)$$

where D is the diffusion coefficient. This relationship shows that species will move from regions of high concentration to regions of low concentration, thereby attempting to balance and mitigate concentration differences. Fick's second law predicts how the concentration of different species can change over time:

$$\frac{\partial c}{\partial t} = -D\nabla_c^2 \quad (8)$$

Convection occurs due to bulk fluid movement influenced by an external force acting on the fluid (pump, blower, stirrer, gravity, pressure gradient, *etc.*). Convection is an important factor that needs to be taken into consideration, as it can significantly enhance mass transport in the system by reducing concentration gradients and promoting a more uniform distribution of reactants. It can be described using the Nernst–Planck equation (eqn (9)), which also accounts for diffusion and migration, defined as the movement of charged species under the influence of an electric field. This equation combines all three mechanisms. It can be expressed as:

$$J = -D\nabla_c - \frac{zF}{RT} Dc\nabla_\Phi - cv \quad (9)$$

where z is the charge state of the ion, v is velocity and ∇_Φ represents the electric field gradient.

One of the advantages of microfluidic devices is the possibility of controlling and varying reactant flow conditions and observing the resulting effects on electrochemical performance, which helps identify and understand mass transport limitations. Microfluidic cell design, combined with precise flow control, is crucial for mitigating mass transfer limitations in traditional system designs. By enabling local convective transport, short diffusion distances, and high surface-to-volume ratios, microfluidic cells significantly improve transport mechanisms. A better understanding of mass transport mechanisms provided by microfluidic cell analysis can lead to significant improvements in the design and functionality of electrochemical devices. Some strategies include the development of novel electrode materials based on important properties (such as wettability, porosity, *etc.*) and optimized electrolyte formulations (viscosity, concentration). Hence, microfluidic systems are beneficial for advancing the study and application of effective mass transport strategies within electrochemical systems.

Applications of microfluidic cells in energy storage systems. Due to their advantages on the small scale and the flow control, which can be useful for understanding different mechanisms, microfluidic systems have many applications where energy storage systems can benefit from their use. Here, we explore the applications of microfluidic cells in electrochemical systems as analytical devices that can drive and speed up the development and optimization of existing energy storage devices, focusing on six major areas: electrochemical analysis, material screening, nanomaterials

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fabrication, interfacial phenomena characterization, cell design, and modelling and simulation.

Electrochemical analysis. Microfluidics facilitates real-time control and monitoring of electrochemical processes, enabling researchers to gather detailed kinetic data, which helps in understanding the mechanisms of energy storage and conversion. Microfluidic cells can be an alternative solution to conventional approaches (*e.g.*, static three-electrode cells) to run electrochemical diagnostic techniques such as cyclic voltammetry (CV) to study reversibility and kinetics, Tafel analysis for kinetic parameter extraction, or electrochemical impedance spectroscopy (EIS) to evaluate kinetics and mass transfer parameters. For that, microfluidic cell designs have been proposed containing a traditional three-electrode configuration so that electrochemical assessment can be done accurately. The three electrodes are: a working electrode, where the primary electrochemical reactions take place; a counter electrode, where current flows to close the electrical circuit; and a reference electrode, which provides a stable and known potential during the experiments. Each of the three electrodes must be interfaced with the same electrolyte in order to facilitate electrochemical cell operation and diagnostics, typically in the presence of flow through a microfluidic channel network. In literature, many microfluidic cells have been proposed as analytical tools for electrochemical property assessments in various energy storage and conversion systems. Some of these microfluidic electrochemical cells are illustrated in Fig. 3.

Lee *et al.*[56] fabricated a flow-through microfluidic fuel cell containing porous electrodes within a microfluidic channel network using two electrolyte flow inlets and one outlet for electrochemical analysis of vanadium redox reactions (Fig. 3a). In the proposed membraneless and catalyst-free three-electrode cell configuration, three carbon electrodes were analyzed as working electrodes (graphite rod, carbon paper, and wet-proofed carbon paper), while a graphite plate was used as counter electrode and a saturated calomel electrode was used as reference electrode. Lee *et al.*[56] conducted electrochemical measurements using V(II) and V(V) vanadium redox electrolytes for conventional electrochemical techniques, such as EIS, Tafel and CV. By running these measurements, they were able to extract important electrochemical properties such as net resistivity, kinetic rates, charge transfer coefficients, and diffusion coefficients. First, EIS was used to estimate the ohmic cell resistance using V(V) electrolyte based on Nyquist plots (semicircle curves based on frequency responses). The first real-axis intercept is known to be the combined ohmic cell resistance (R_s), which accounts for contact, solution, and electrode resistances. Under fixed conditions (electrolyte concentration, electrode dimensions, and electrical connections), the electrode resistance (R_{net}) can be calculated by subtracting both contact and solution resistances from R_s. Tafel analysis was used in order to extract kinetic parameters for both V(II) and V(V) electrolytes. Kinetics and ohmic overpotentials were decoupled using IR compensation, so that parameters such

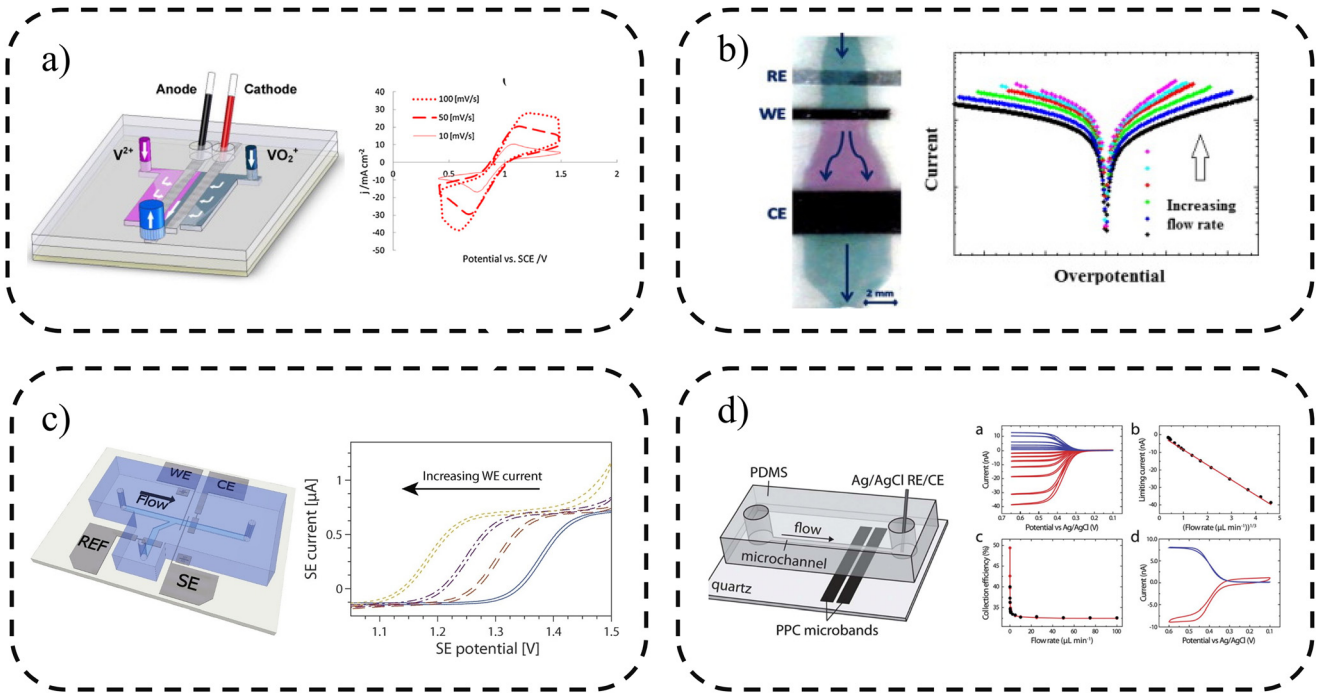

Fig. 3 Microfluidic electrochemical cells used to analyze: a) electrochemical characteristics of vanadium redox reactions on porous carbon electrodes. The image is reproduced from ref. 56 with permission from Elsevier, copyright 2012. b) Electrochemical kinetics in flow-through porous electrodes. The image is reproduced from ref. 57 with permission from Elsevier, copyright 2015. c) High current density experiments. The image is reproduced from ref. 61 with permission from Elsevier, copyright 2017. d) Electrocatalyst kinetics. The image is reproduced from ref. 64 with permission from Royal Society of Chemistry, copyright 2012.

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as exchange current density and charge transfer coefficient could be evaluated for both electrolytes. Those parameters were calculated based on the *y*-intercept and slope of the obtained Tafel curves. The rate constant (k_0) was also calculated from the measured data.[138] Lastly, CV was used to investigate the reversibility of both V(II)/V(III) and V(IV)/V(V) redox couples based on their respective peak potentials, and diffusion coefficients were calculated from the peak potential and peak current intensity of the voltammograms. Cell polarization curves were also obtained experimentally, and were in agreement with numerical simulation results obtained from the proposed model by the authors.

Goulet *et al.*[57] measured electrochemical reaction kinetics using a flow-through porous electrode microfluidic cell fabricated by soft lithography in PDMS (Fig. 3b). The proposed cell contained a straight microfluidic channel with a single inlet and a single outlet for the electrolyte flow and three electrodes: carbon paper (both working and counter), and a saturated calomel electrode (reference). For electrochemical measurements, V(II)/V(III) or V(IV)/V(V) redox electrolyte was pumped into the cell using a syringe pump and removed by another syringe pump at the outlet. Electrochemical analyses were done in order to understand kinetics parameters, using Tafel curves and EIS measurements. The exchange current densities and rate constants for both vanadium electrolytes on carbon paper electrodes were extracted from the Tafel curves, and the results were compared. It was shown that the V(II)/V(III) reactions on the negative electrode were sluggish reactions, having rate constants two orders of magnitude lower compared to the V(IV)/V(V) redox couple, therefore being the limiting reaction for vanadium redox flow batteries. Note that the microfluidic cell design proposed by Goulet *et al.*[57] tackled mass transport effects observed from the previously designed cell by Lee *et al.*,[56] showing that stirring the solution is not effective for replenishing reactants at the electrode surface.

Ingdal[58] also proposed a microfluidic flow cell for electrochemical reaction evaluation using a four-electrode cell configuration, having two working electrodes (working and working sense). The proposed cell was fabricated using photolithography and used different working and counters electrodes such as a gold–platinum, titanium–platinum, and iodine–coated platinum electrodes, and an external reversible hydrogen reference electrode. Two redox couples were studied, namely ferrocyanide/ferricyanide and ruthenium hexamine(II/III), and CV and EIS measurements were performed to evaluate the reversibility of the reactions. However, the EIS analysis was restricted by low reproducibility from open-circuit potential fluctuation. Møinichen[59] used a similar microfluidic flow cell for electrochemical reaction studies based on the same external hydrogen reference electrode and platinum electrode cell design proposed by Ingdal. While Ingdal[58] focused on the electrode composition and reference electrode position and their impact on electrochemical measurements, Møinichen[59] focused on the effects of electrode thickness and flow channel height using the ruthenium hexamine(II/III) redox couple in sulphuric acid supporting electrolyte. The obtained CV and EIS measurements provided useful information on the effects of flow rate, sweep rate, and oxygen content in the electrolyte on the electrochemical performance. Other examples include three-electrode microfluidic cells for low-current electrochemical detection, which were able to evaluate kinetics and reversibility parameters based on CV results,[60] and a microfluidic cell with integrated palladium–hydride (PdH) reference electrode for high current density experiments (Fig. 3c), able to characterize electrochemical performance up to 4 mA cm^{-2}.[61]

Microfluidic cells can also be applied in combination with other characterization tools in order to provide a broader assessment. Jhong *et al.*[62] combined results from *in situ* microfluidic cell experiments with *ex situ* micro-X-ray computed tomography (MicroCT) images to understand the correlation between physical properties and electrochemical performance of fuel cell electrodes. While polarization curves were extracted from electrochemical measurements using the proposed microfluidic cell, GDL structural analysis (layer thickness, internal architecture, and interfaces) was done based on MicroCT images. By combining these two techniques, they were able to elucidate the correlation between fuel cell performance and electrode compression. Gas evolution on the electrode surface was studied and observed by Shyu and Huang[63] using their proposed hydrogen peroxide microfluidic cell. By analyzing polarization curves, they were able to evaluate the impact of gas bubbles on system performance by varying the microchannel width and volumetric flow rate. Current density and ohmic loss characteristics were evaluated for performance comparison. Other than diagnosing the electrochemical performance, they also visualized bubble formation in the microfluidic cell using a high-speed video camera, showing the advantage of combining microfluidic cells with imaging techniques for gas evolution assessment.

Microfluidic cells were also employed to characterize electrocatalyst activity. Dumitrescu *et al.*[64] proposed a microfluidic cell for examining the kinetic properties of electrocatalyst materials (Fig. 3d). The proposed device consisted of two pyrolyzed photoresist carbon (PPC) microbands enclosed within PDMS microchannels in a three-electrode configuration, where the PPC microband was used as working electrode with a gold wire as counter electrode and a Hg/Hg_2SO_4 electrode as reference electrode. For electrochemical measurements, ferrocene methanol (FcMeOH) in aqueous KNO_3 was used as electrolyte and different electrochemical parameters were evaluated such as limiting current density, collection efficiency, rate constant, and mass transport coefficient. Electrochemical kinetics evaluation was also performed on Pt electrodes for the oxygen reduction reaction (ORR) using CV and linear sweep voltammetry (LSV) techniques and compared to rotating ring disk electrode (RRDE) results. It was shown that the proposed microfluidic cell offers several advantages over conventional rotating disk electrodes, such as higher collection efficiency (97%), a broader range of mass transfer coefficients (up to 0.5 cm s^{-1}), a wider temperature operating window (up to 70 °C), and reduced sample

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preparation. Fanavoll[65] used a six-electrode microfluidic cell to study the oxidation of formic acid and formaldehyde on palladium. For that, a PDMS microfluidic cell was fabricated using four 100 μm working electrodes, a 500 μm counter electrode, and a 1 mm PdH thin-film reference electrode. Both H_2SO_4 and $HClO_4$ were used as electrolytes to evaluate Pd and Pt working electrodes and understand their catalytic activity. Peaks related to hydrogen adsorption/desorption and platinum and palladium oxide formation were investigated. Electrochemically active surface area (ECSA) was also calculated based on surface charge. Brushett *et al.*[66] proposed an alkaline microfluidic H_2O_2 cell as a platform for both catalyst and electrode characterization. A modular microfluidic fuel cell was fabricated using polymethylmethacrylate (PMMA) and polytetrafluoroethylene (PTFE) containing Pt/C or Ag/C were used as cathode, while Pt/C was used as anode. The proposed design had a circulating alkaline electrolyte to facilitate long-term electrode durability studies. The authors used this setup to evaluate the influence of various parameters such as PTFE weight percentage and the catalytic effects of Ag and Pt on fuel cell performance. Polarization curves and EIS measurements were performed in order to understand kinetics and mass transport parameters. The correlation between PTFE amount and flooding was elucidated, as well as its impact on both kinetics and mass transport. Cathodic potential losses attributed to oxygen reduction activity was also investigated using the proposed microfluidic cell and further work on long-term carbonate formation and the impact of corrosive media on electrode performance was suggested.

As demonstrated in the studies above, microfluidic cells show strong potential as analytical tools for a wide range of electrochemical systems, providing valuable insights into electrode and electrolyte behavior. Their ability to incorporate controlled fluid flow and systematically vary electrolyte parameters (velocity, concentration, temperature, *etc.*) enables detailed evaluation of kinetics and mass transport limitations for different materials and chemistries. By scaling down complex systems, microfluidic cells allow faster, more controlled, and cost-effective experiments compared to traditional methods, while enabling more realistic studies of transport phenomena that are often oversimplified in conventional characterization tools.

Material screening. Researchers use microfluidics for material screening in energy storage systems because it provides a systematic method for accelerating the discovery and optimization of new materials, which is vital for improving the performance and efficiency of batteries, fuel cells, and other electrochemical energy storage and conversion systems. Microfluidic cells enable rapid generation of data on how different material compositions respond to various electrochemical conditions, allowing researchers to swiftly identify optimal candidates for energy storage applications. Numerous studies on catalyst materials have been reported that utilize some of the microfluidic cells designs discussed previously as analytical tools focusing now on material screening, as summarized in Table 1 and showcased in Fig. 4.

Ahmad *et al.*[67] studied the effects of low-loading supported Pt/Ru and Pt on XC-72R electrodes in the performance of a microfluidic direct methanol fuel cell. Their study aimed to improve cell efficiency and power output using small active area and low catalyst loading. Using the fabricated microfluidic cell, they were able to correlate catalyst loading to cell performance and determine the

Table 1 Summary of catalyst screening and performance assessment using microfluidic cells

Fuel cell	Catalyst	Support	Catalyst loading	Power density	Ref.
Methanol	Pt/Ru	XC-72	5 mg cm^{-2}	14.0 mW cm^{-2}	67
	Pt	CNTs	—	5.70 mW cm^{-2}	68
	CoPc–Pt	XC-72	0.35 mg cm^{-2}	—	69
Hydrogen	NiO–Ni	CNT	4.1 mg cm^{-2}	40.0 mW cm^{-2}	70
	Pt	—	—	22.1 mW cm^{-2}	71
	$NiFe_2O_4$	XC-72	1.55 mg cm^{-2}	—	72
Ethanol	PdAg	MWCNT	—	14.5 mW cm^{-2}	73
	KS6/super P	—	—	0.09 mW cm^{-2}	74
	Pt–Sn–Eu	XC-72	1–2 mg cm^{-2}	8–10 mW cm^{-2}	75
Formic acid	Pd	MWCNTs	0.7 mg cm^{-2}	2.9 mW cm^{-2}	76
	Pd–Ni_2P	XC-72	6 mg cm^{-2}	550 mW cm^{-2}	77
	Pd	—	0.42 mg cm^{-2}	35.8 mW cm^{-2}	78
Glucose	Au	XC-72	—	0.5 mW cm^{-2}	79
	Au	MWCNT	—	0.28 mW cm^{-2}	80
	AuAg	XC-72		0.51 mW cm^{-2}	81
Vanadium	N-doped TiO_2	—	3 mg cm^{-2}	—	82
	Ti_2O_3	—	1 mg cm^{-2}	—	83
	Self-doped TiO_2	—	1 mg cm^{-2}	—	84
Ammonia	Ni	—	~5 mg cm^{-2}	8.43 mW cm^{-2}	85
	NiCu	CNT	2.3 mg cm^{-2}	10.94 mW cm^{-2}	88
	Ni	CNT	20 mg cm^{-2}	6.6 mW cm^{-2}	89
Hydrogen peroxide	Prussian blue	rGO	5 mg cm^{-2}	2.22 mW cm^{-2}	86
	Pt/Pd	—	5 mg cm^{-2}	30.0 mW cm^{-2}	90
	Ni-Prussian blue	MWCNT	4 mg cm^{-2}	14.41 mW cm^{-2}	91

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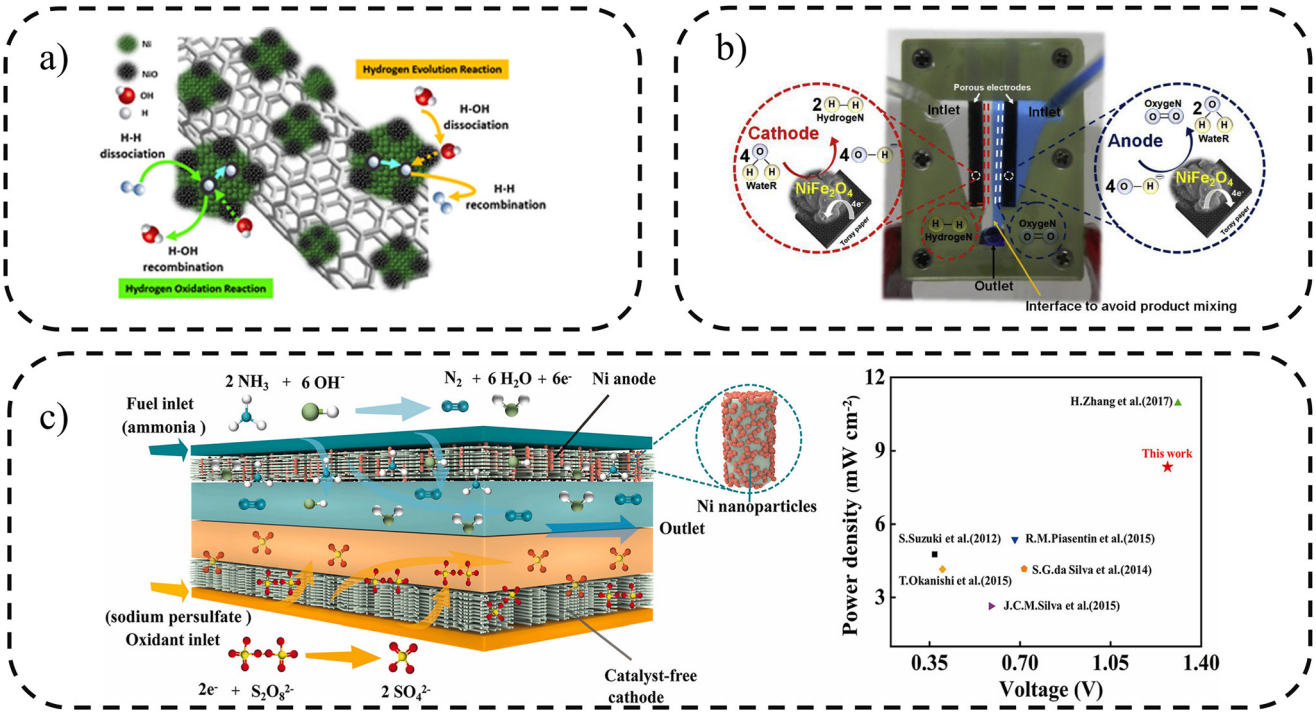

Fig. 4 Modified electrodes used in microfluidic cells for catalyst screening and performance evaluations. a) NiO–Ni catalyst on CNTs as hydrogen bifunctional electrode. The image is reproduced from ref. 70 with permission from American Chemical Society, copyright 2020. b) 3D $NiFe_2O_4$ hollow spheres for water splitting. The image is reproduced from ref. 72 with permission from Elsevier, copyright 2019. c) Ni catalyst materials for low cost and high-performance direct ammonia fuel cells. The image is reproduced from ref. 85 with permission from Elsevier, copyright 2024.

optimal catalyst loading for both anode and cathode sides. Based on results from peak power density curves, they demonstrated a microfluidic cell with high power density compared to other cells in the literature. Huo *et al.*[68] studied carbon nanotubes (CNTs) aided by platinum nanoparticles as catalyst materials using a Y-channel microfluidic direct methanol fuel cell and the influence of catalyst layer materials and deposition methods on the microfluidic cell performance. For that, they compared the performance of different Pt/CNTs coated electrodes and pure Pt electrode, aiming to highlight the advantages of using CNTs as support. CV results confirmed the enhancement in the ECSA for CNTs supported electrodes, which also showed improvements in cell performance verified by increased peak power densities. Thus, this study showed the opportunities associated with the use of microfluidic cells for catalyst layer optimization based on catalyst material and support selection. Lu and Reddy[69] investigated the electrochemical performance of cobalt phthalocyanine (CoPc) as a prospective cathodic catalyst in methanol fuel cells. Based on both chemical and electrochemical characterization of the proposed catalyst materials, they evaluated the correlation between catalyst composition and deposition temperature and its impact on electrochemical performance. Based on the results, it was revealed that cobalt increased the electrocatalyst activity for the methanol oxidation reaction and improved to the tolerance of methanol poisoning, which can be beneficial to conventional Pt/C electrodes used in methanol fuel cells.

Campos-Roldán *et al.*[70] examined the applicability of NiO–Ni nanoparticles supported on CNTs as an electrode catalyst for unitized regenerative alkaline microfluidic cells (Fig. 4a). NiO–Ni nanoparticles were proposed since they do not require complex synthesis and have been widely applied as hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) electrocatalysts. An electrochemical assessment was carried out to evaluate NiO–Ni kinetic parameters and the results indicated that electrochemical performance improvements were linked to the synergistic effect of Ni (offering sites for adsorption and dissociation of hydrogen) and NiO (enhancing the Volmer reaction rate), along with modifications to the electronic properties of the support. Electrochemical performance results for maximum power density and consumed power density were compared to benchmark commercial materials and the proposed catalyst composition showed potential application as a bifunctional catalyst for both fuel cell and electrolyzer applications. Omosebi and Besser[71] fabricated and tested an in-membrane micro fuel cell using conventional Pt and Pt/C catalyst layers. In the novel in-membrane design, both catalyst layer and flow channels were integrated into the Nafion membrane, which can lead to lower material usage, low weight, and high energy density. The cell performance was evaluated for both Pt and dispersed Pt/C thin film catalysts under dry and humidified conditions. The results indicated that sputtered Pt electrodes can improve power density under mitigated operating conditions (relative humidity). However, the microfluidic cell was limited by ohmic

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resistance, which was still very significant. Therefore, more work is required to improve cell performance, with opportunities for new cell designs and architectures, which is also one of the applications of microfluidic cells discussed later in this article. Martínez-Lázaro *et al.*[72] utilized 3D $NiFe_2O_4$ hollow spheres as catalyst materials for water splitting in an alkaline microfluidic system (Fig. 4b). $NiFe_2O_4$ was chosen for its large surface area, good stability, and catalytic activity for the oxygen evolution reaction (OER) compared to conventional IrO_2 catalyst materials. Electrochemical assessment was made for both performance evaluation (mainly hydrogen production) and stability. The results demonstrated that $NiFe_2O_4$ has comparable hydrogen production rates to IrO_2 (25.76 *vs.* 27.10 μg s^{-1}), highlighting its potential as a platinum group metal-free catalyst material.

Armenta-González *et al.*[73] investigated Pd and PdAg nanoparticles on multiwall (MW) CNTs as prospective catalyst materials for microfluidic ethanol fuel cell applications. The results showed good activity and electrochemical performance for both catalyst materials, and high power densities. The higher power density for PdAg/MWCNTs was attributed to a larger ECSA, which may have contributed to enhanced catalyst properties. The results were also compared to various studies in the literature, where their PdAg/MWCNTs electrodes exhibited competitive outcomes, which opens opportunities to explore new catalyst materials for ethanol fuel cells. Selloum *et al.*[74] examined the performance of the first microfluidic ethanol biofuel cells using bioelectrodes activated with carbon nanoparticles in a Y-shaped microfluidic channel. They analyzed the bioelectrocatalytic process for different carbon nanoparticles (SuperP and KS6). Their findings indicated that carbon nanoparticles enhance bioelectrocatalytic activity, diffusion, and electron transfer due to their high porosity and surface area, serving as effective hosts for redox species. Corradini *et al.*[75] looked into the application of rare earth elements as anodes in direct ethanol fuel cells. For this purpose, Pt–Sn–Eu/C catalysts were synthesized and compared to commercial Pt/C and Pt–Sn/C catalysts. The Pt–Sn–Eu/C catalyst demonstrated improved electrochemical performance, with higher oxidation current density and lower oxidation potential. This enhanced performance was attributed to the Sn/Pt–Eu electronic effect, which weakens the absorption of intermediate products and favours the electrooxidation reaction (EOR) mechanism. The role of Eu was noted to increase the electrocatalytic activity for the EOR.

Morales-Acosta *et al.*[76] presented the performance evaluation of Pd/MWCNTs as catalysts for formic acid fuel cell applications. Electrochemical investigations were carried out and results revealed a higher power density using MWCNTs as support, in contrast to values reported in the literature with XC-72. Performance improvements were attributed to the superior electronic properties of MWCNTs combined with improved particle distribution. Chang *et al.*[77] examined the effect of Pd–Ni_2P/C as an anode catalyst material for direct formic acid fuel cells, reporting a power density 3.5 times higher than state-of-the-art Pd/C commercial catalyst materials. The high performance, activity, and stability of Pd–Ni_2P/C marked it as a competitive catalyst material for direct formic acid fuel cell applications. Zhou *et al.*[78] assessed the Pd nanoarray catalyst for the same anode application and showed that Pd-nanoarray coated on carbon papers electrodes achieved power densities nearly 50% higher than conventional Pd-black anodes. This enhanced performance can be attributed to improved charge and mass transport rates, high electrocatalytic activity, and great stability, along with the electrode superaerophobicity, which facilitates rapid gas bubble release.

Guerra-Balcázar *et al.*[79] synthesized and evaluated the performance of Au/C and Au/Pani catalyst materials for anode electrodes in microfluidic glucose fuel cells. Electrochemical performance evaluation was carried out and the results revealed that Au/C/Pt electrodes showed higher power densities compared to Au/Pani, possibly due to the interaction of particle/support and the ECSA : Au loading for Au/C, which was six times higher than for Au/Pani. The performance was benchmarked against other results reported in the literature, with Au/C electrodes exhibiting the highest performance among the electrochemical systems reviewed. Furthermore, Guerra-Balcázar *et al.*[80] studied Au/MWCNTs as catalyst support in microfluidic glucose fuel cells, and showed that CNTs offer advantages over conventional carbon supports, such as chemical stability and effective metal dispersion on the MWCNT surface. This was reflected in the performance results, where Au/MWCNTs showed 80% performance enhancement compared to Au/C. López-González *et al.*[81] researched laccase/C as a biocathode and AuAg/C as an inorganic anode for a hybrid microfluidic glucose fuel cell. Laccase was selected for its cost-effectiveness, as it is derived from agricultural residues and serves as a viable catalyst alternative. A power density of 0.45 mW cm^{-2} was achieved using a Vulcan XC-72 ABTS laccase electrode, which was able to operate for four days during dry storage, demonstrating competitive power density relative to other hybrid fuel cells in the literature.[81]

Various catalyst applications in other electrochemical systems were also reported, including diverse Ti catalyst materials as photoanodes for all-vanadium photoelectrochemical cells, such as N-doped TiO_2,[82] Ti_2O_3,[83] and self-doped TiO_2,[84] nickel nanoparticles for direct ammonia microfluidic fuel cells (Fig. 4c),[85] reduced graphene oxide and Prussian blue for hydrogen peroxide fuel cells,[86] and various Cu catalyst materials for microfluidic electrolyzers.[87]

Microfluidic cells offer a powerful platform for catalyst material screening, particularly when cost and material availability are key considerations. Their scaled-down configuration enables systematic testing of diverse catalyst compositions and supports across various electrochemical systems, allowing performance evaluation with minimal material usage. This approach can accelerate the discovery of efficient, low-cost alternatives to conventional, expensive materials such as platinum and other precious metals commonly used in large-scale applications.

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Table 2 Representative nanocatalyst materials with different compositions and structures synthesized by microfluidic systems

Flow	Composition	Structure	Ref.
Continuous	Ag	Nano spheres, nanodecahedra, nanoplates	93
Continuous	Au/Ag	Nanorods	94
Segmented	Au	Nanospheres, nanorods, sharp-edged	95
Segmented	Pt–Si	Decorated nanospheres	96
Continuous	Pd/PdPt	Nanocubes	97
	PdPt	Core–shells	
Continuous	Pt	Nanoparticles	98
Continuous	Pt/Pd/Au	Nanoparticles	99
	Pt/PtPd/PtNi/PtCo/PtRu	Nanodendrites	
	Pt/PtPd	Nanocubes	
	Pd	Nanosheets, nanorods	
	Pt–Pd	Decorated nanoparticles, nanowires, core–shells	
	PdAu	Nanoparticles	
	Ag–Pd	Semi-Janus, nanowires, core–shells	
	Pd–Au	Nanodumbells, nanostars	
Continuous	CeO_2	Nanoparticles, nanorods, nanocubes	100
Segmented	TiO_2	Microspheres	101
	CeO_2	Nanospheres	
	ZnO	Aggregates	

Nanomaterials fabrication. Microfluidic systems are highly effective for fabricating nanoparticles due to their ability to control fluid flow at the microscale, enabling precise manipulation of reaction conditions. One significant advantage is the enhanced control over synthesis parameters such as concentration, temperature, and reaction time, which leads to uniform and consistent particle size and shape. These features facilitate innovative approaches for creating multifunctional nanoparticles that meet the demands of modern technologies. Various catalyst materials with complex compositions and structures have been documented in the literature, as summarized in Table 2 and illustrated in Fig. 5.

Castillo-Vallés *et al.*[92] used a coaxial microfluidic system for a rapid and controlled method of organic nanotubes

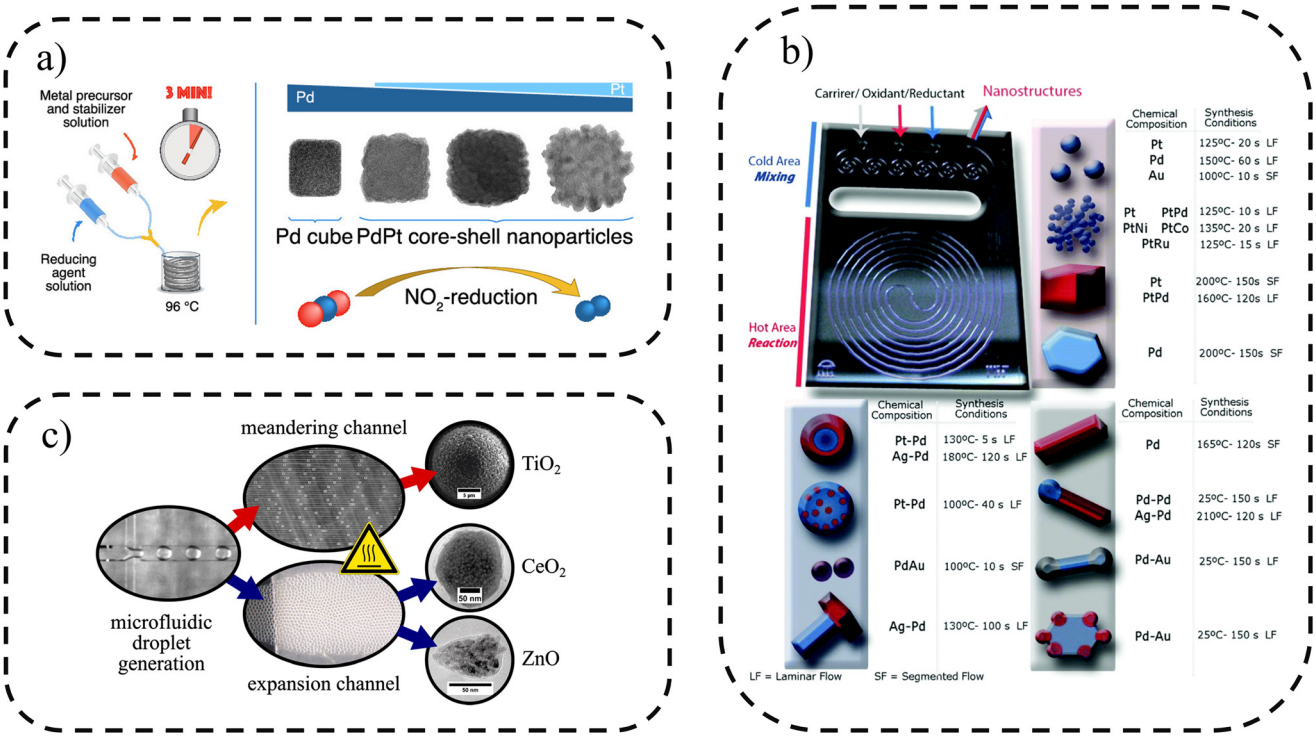

Fig. 5 Nanocatalyst materials fabricated *via* microfluidic systems. a) Core–shell nanoparticles. The image is reproduced from ref. 97 with permission from American Chemical Society, copyright 2019. b) Metallic and bimetallic catalysts with different nano structures. The image is reproduced from ref. 99 with permission from Royal Society of Chemistry, copyright 2016. c) Metal oxide nanoparticles synthesized using a nonaqueous microfluidic approach. The image is reproduced from ref. 101 with permission from Elsevier, copyright 2018.

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preparation. The coaxial device had an inner microcapillary containing organic phase and an outer microcapillary supplying the aqueous phase, which were later mixed to cause the aggregation of the compound, resulting in nanostructures. They were also able to combine organic nanotubes with gold nanoparticles for the preparation of nanocomposites with enhanced properties. These findings are important to explore the use of microfluidic systems for nano catalyst preparation for many electrochemical systems. Given the rapid and cost-effective (low consumption of reactants) nature of the method, it could also be useful to screen different synthesis parameters (concentration, temperature, pH, *etc.*) for nanoparticle production. Silvestrini *et al.*[93] showed the growth of shape-selective Ag nanoparticles using a microfluidic system for photochemical nucleation with LED light. They synthesized nanoparticles with three different shapes (platelets, decahedra, and spheres) by varying the irradiation wavelengths. Although the preparation of Ag nanoparticles was successful, more work is needed to produce homogeneous samples and control the growth process. Boleininger *et al.*[94] developed a method for rod-shaped Au and Ag nanocrystals using a continuous flow microfluidic system. The proposed method mixed a growth solution and a seed solution that were flowed through a temperature-controlled tubing for crystal growth. The system also offered an online optical monitoring system for the reproducible and controlled synthesis of nanoparticles with specific shapes based on synthesis variable inputs (growth temperature, growth and seed solutions ratio, *etc.*). However, more research is needed to understand the influences of different parameters such as reaction temperature and pathway on the nanoparticle production. Duraiswamy and Khan[95] utilized a droplet-based microfluidic system for the synthesis of anisotropic Au nanocrystals. In the proposed method, Au nanoparticle seeds and growth reagents were mixed by chaotic advection in a T-junction microfluidic system, forming a stable stream for particle formation. Three different shapes (spherical, rods, and extended sharp-edged) were achieved by tuning reagent concentrations and flow rates. However, further work is necessary to enable a fully continuous process. This research also opens possibilities for synthesizing dispersions of different metal nanocrystals, as they employed the same ink formulation (metal precursor, solvents, and surfactants).

Lee *et al.*[96] prepared metal-decorated nanoparticles using a microfluidic method. By using a silicon microreactor, they were able to synthesize Pt nanoparticles onto iron oxide/silica core–shell nanospheres and assemble them into spherical micron-sized particles using a microfluidic drop generator. Catalyst performance was evaluated for aldehyde oxidation applications and showed good catalytic activity compared to two commercial noble metal catalysts (Pd/C and Pt/Al_2O_3). The high performance can be attributed to the uniform distribution of the catalyst, which facilitates access for reactants to active sites, as well as the irregular shape of the support materials, which aids in flow channelling. Pekkari *et al.*[97] synthesized Pd nanocubes and PdPt core–shell nanoparticles for NO_2 reduction using a continuous microfluidic system (Fig. 5a). The microfluidic reactor featured an injection stream with Pd precursor solution with cetyltrimethylammonium bromide (CTAB) that was mixed with a reducing agent before being heated to form Pd nanocubes. With the proposed synthesis method, uniformly shaped nanoparticles were prepared in merely 3 min. These nanoparticles exhibited high catalytic activity towards NO_2 reduction, along with good thermal stability at both low ($<$136 °C) and high temperatures. Although this work focused on the NO_2 application, both Pd and Pt are used in many different energy storage and conversion systems, which could benefit the further utility of this method. Laura *et al.*[98] prepared Pt-based heterogeneous catalyst using microfluidic systems for volatile organic compounds (VOC) abatement applications. The synthesis procedure was proposed for a fast and controlled production based on two main stages: (1) pumping and mixing reactants before the crystallization stage and (2) reacting stage using a PTFE tubing loop in a thermostatic bath to promote (and tune) crystallization. Using the proposed microfluidic systems, they synthesized ultra-small Pt nanoparticles and Pt alloys such as PtPd, PtRu, and PtRh deposited on SBA-15 support. Compared to traditional bath production, to the microfluidic method reduced the synthesis time from 18 min to 90 s and doubled the productivity to 27 mg Pt nanoparticles per hour. The prepared nanoparticles also showed good catalytic activity for n-hexane oxidation, showing total removal and no catalytic deactivation for 30 h duration. Sebastián and Jensen[99] reported a versatile synthesis platform for a broad metallic and bimetallic nanostructure using a microfluidic reactor (Fig. 5b). The proposed microreactor can withstand significant pressures (6 MPa) and temperatures (350 °C) and its design was based on two zones: cold area (mixing) and hot area (reaction). The proposed design had a spiral channel to prevent solid accumulation and the flow pattern could also be switched from laminar to segmented flow to avoid dispersion problems. By using a facile, fast, and shape-selective synthesis process, they were able to prepare Pt, Pd, and Au metal nanoparticles and bimetallic particles combining these elements with different shapes. Moreover, they synthesized new complex nanostructures such as Pt–Ru, Pt–Ni, and Pt–Co nano dendrites, Pt–Pd heterostructures, Ag–Pd core–shells, Au–Pd nano dumbbells, and Au–Pd nanosheets. This work provided an insightful contribution for nanoparticles production with size, shape, and metal distribution control, which is essential for catalyst production for various energy storage systems.

Yao *et al.*[100] showed the ultrafast, continuous and shape-controlled production of CeO_2 nanostructures using a microfluidic system. Compared to traditional batch production, CeO_2 nanorods and nanocubes were synthesized in 8 min using a homemade microfluidic system where cerium nitrate aqueous solution (continuous phase) was pumped and mixed with sodium hydroxide (dispersed phase) in a T-shaped micro-mixer.

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The mixture was then flowed into a micro-reactor and heated from 100 °C to 230° for crystallization. The effects of temperature and sodium hydroxide concentration on particle size and shape were investigated, and it was shown that different CeO_2 shapes were achieved (cubes and rods). Both structures were evaluated for H_2O_2 decomposition application, and showed 0.78- and 1.8-fold improvements in catalytic activity compared to nanoparticles attributed to variations in superficial oxygen vacancy concentration. This work was significant in demonstrating the potential of rare earth metal oxides, commonly used in various redox catalytic applications, as an alternative catalyst material to noble metal nanoparticles. Stolzenburg *et al.*[101] successfully synthesized three metal oxide nanoparticles using a microfluidic droplet-based system. TiO_2, CeO_2, and ZnO particles were prepared *via* a nonaqueous sol–gel method, allowing for precise and rapid control over the nanoparticle preparation (Fig. 5c). Temperature, reaction zone, and organic content played important roles in forming the metal oxide particles and must be considered for catalyst preparation. This work provided valuable information that can be applied to various metal oxides for controlled and high-quality nanoparticle synthesis.

Microfluidic cells present a powerful alternative for catalyst material fabrication, offering precise control over synthesis parameters such as reactant concentration, temperature, pH, flow rate, and residence time. This high degree of control enables the production of catalysts with tailored size, morphology, and composition, which are critical for optimizing electrochemical activity and stability. Their rapid, streamlined, and cost-efficient synthesis processes minimize reagent use and waste generation, making them ideal for exploring large libraries of candidate materials, including novel, earth-abundant alternatives to costly platinum-group metals. Furthermore, the continuous-flow nature of microfluidic systems facilitates reproducibility and scalability of optimized synthesis routes, bridging the gap between laboratory-scale discovery and practical deployment in next-generation electrochemical systems.

Interfacial phenomena characterization. Microfluidic systems are essential for providing a platform for the detailed characterization of interfacial phenomena and their correlation to electrochemical performance, which is crucial for optimizing electrode and electrolyte interactions in electrochemical cells. By using microfluidic cells, researchers can closely examine key factors such as wettability, ion transport across boundaries, catalyst performance, gas evolution, and the assessment of crossover effects, as shown in Fig. 6. Therefore, leveraging microfluidic systems for characterizing interfacial phenomena, including crossover effects, offers a deeper understanding of fundamental processes, driving innovations in the design and performance of energy storage technologies.

Goulet *et al.*[23] employed a three-electrode analytical microfluidic cell to evaluate the impact of electrode wettability on electrochemical performance and explain the discrepancy of

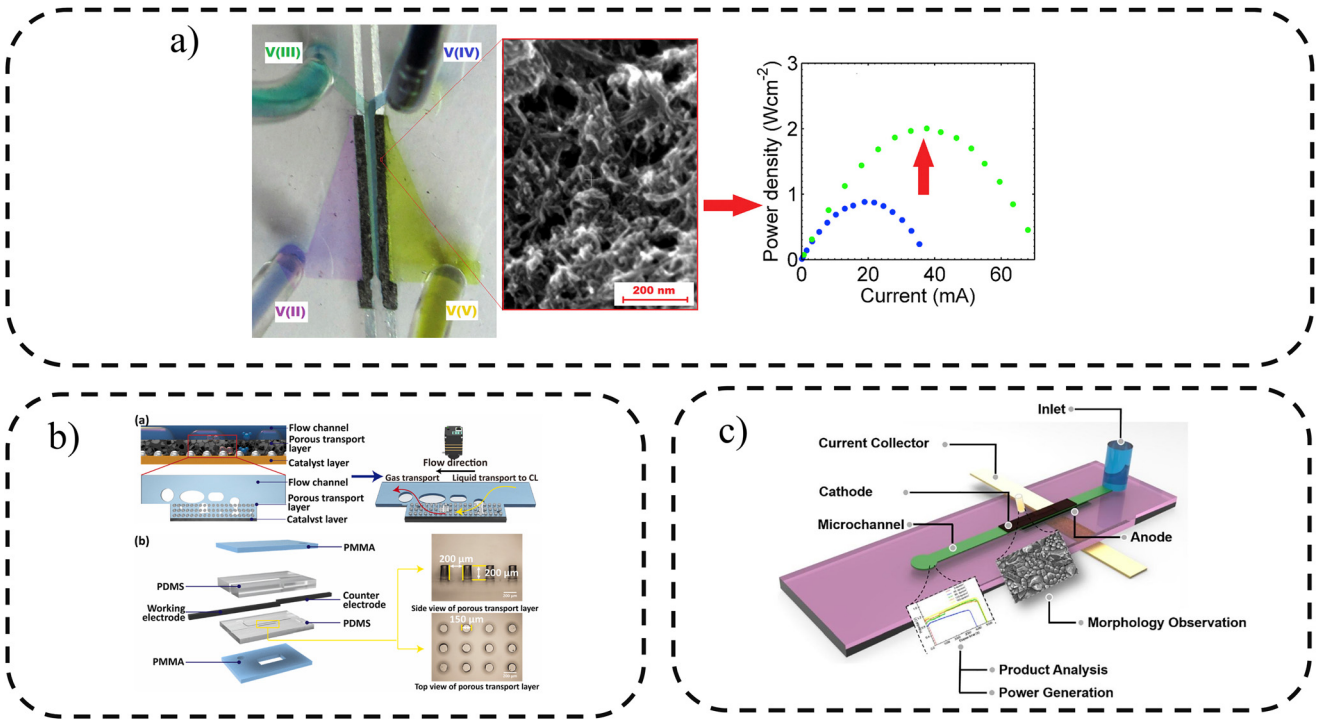

Fig. 6 Microfluidic cells used to characterize and understand interfacial phenomena. a) *In situ* flow deposition for improved kinetics and mass transport in aqueous electrochemical flow cells. The image is reproduced from ref. 102 with permission from Elsevier, copyright 2017. b) Gas evolution in water electrolyzers. The image is reproduced from ref. 107 with permission from Elsevier, copyright 2023. c) Effect of shear force and microenvironment on electrode morphology and its correlation to electrochemical performance. The image is reproduced from ref. 109 with permission from Elsevier, copyright 2022.

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reaction rates found in literature. They demonstrated that electrode properties such as porosity and wettability affect the perceived kinetic rates, which can sometimes be misinterpreted in conventional static electrochemical testing. In order to extract quantitative and qualitative data and draw more meaningful conclusions, they suggested utilizing alternative techniques, such as EIS in combination with CV using flow cell techniques, to gain a better understanding of electrode performance, as these methods can account for the ECSA while eliminating diffusion interference. These results provide valuable insights into electrode characterization and the correlation between electrode properties and electrochemical performance. Goulet *et al.*[102] also proposed an *in operando* catalyst deposition method to maximize power density based on the co-laminar microfluidic cell described earlier (Fig. 6a). By dispersing CNTs in the vanadium redox electrolyte and flowing it through the microfluidic cell, the catalyst was dynamically deposited during operation. They identified an equilibrium where catalyst deposition peaks when deposition and detachment are no longer observed, enhancing the electrode's electrochemical surface area and pore size distribution. Performance results showed an increase in power density for the dynamic CNT deposition method compared to the baseline due to improved wetted surface area and mass transport. The proposed catalyst deposition method can be an effective alternative for traditional methods since it is rapid, high performing, and adaptable for various flow cells.

Brushett *et al.*[103] also examined the performance of various Pt/C electrodes using a flowing electrolyte alkaline fuel cell as an analytical platform and elucidated the relation between performance and electrode preparation procedures (hot pressing, acclimatization). The proposed microfluidic H_2/O_2 fuel cell had an alkaline electrolyte stream flowing separately from both hydrogen and oxygen streams, two gas diffusion electrodes, and a reference electrode for electrode performance monitoring and assessment based on power output. The results indicated that the anode performance is influenced by electrode properties (compression, hydrophobicity) and electrolyte characteristics (conductivity, viscosity). The findings revealed a negative effect on hot-pressed anodes linked to the water management process influenced by changes in porosity and, subsequently, hydrophobicity. When analyzing the trade-off between electrolyte concentration, kinetics, and viscosity, it was noted that anodes perform poorly at low concentrations due to the restricted availability of hydroxyl ions. At higher concentrations, the electrolyte viscosity increases and limits transport processes, leading to decreased performance. These findings and the proposed technique for assessing electrode performance show important utility for the advancement of alkaline flow cells and other electrochemical systems. Jhong *et al.*[104] evaluated and compared different catalyst deposition methods (hand painting, air brushing, and screen printing) and their effects on catalyst layer morphology and electrode performance. By combining structural analysis using microCT and a microfluidic cell for *in situ* electrochemical performance assessment, they were able to correlate changes in electrode performance and catalyst layer structure. The study revealed that catalyst distribution uniformity and particle agglomeration significantly influence electrode performance, with air brushing achieving the highest performance and reproducibility among the methods. These findings demonstrate how understanding catalyst materials deposition can enhance overall cell performance, which many electrochemical systems could benefit from.

Brushett *et al.*[105] studied Pt-based catalyst performance, durability, and stability using a microfluidic H_2O_2 cell based on the previously reported microfluidic device,[103] where the electrochemical characterization was carried out using commercial unsupported Pt and Pt_3Co as well as *in house* chemically treated Pt_3Co and Pt_3Co/Mo as working electrodes. The proposed microfluidic cell can be crucial for catalyst material screening as it can be used for accelerated aging and durability studies, varying a range of conditions (electrolyte pH, flow rate and composition) and eliminating fuel cell limitations such as water management and removal. Moreover, it can also advance low-cost catalyst materials development, which is a key obstacle for commercialization and adoption of fuel cell technologies. Zhang *et al.*[106] studied the impact of catalyst loading on paper-based microfluidic fuel cells and scaling-up strategies for direct ethanol paper-based microfluidic fuel cells. To mitigate the high cost of noble catalysts, they controlled the anode catalyst loading and revealed that a loading of 1 mg cm^{-2} exhibited optimum cost/performance based on power density results.

Xu *et al.*[107] fabricated a microfluidic cell to mimic the porous transport layer (PTL) of a proton exchange membrane (PEM) water electrolyzer and understand the oxygen evolution reaction at the anode (Fig. 6b). The influence of current density on bubble formation was observed using a microfluidic reactor, and it was shown that a greater number of bubbles appeared as the current density increased. A higher volume of bubbles can enhance gas phase saturation and, consequently, mass transport resistance, which can reduce cell performance. It was also demonstrated that the detachment of bubbles can be improved by increasing the flow rate. This work provided an important contribution on how microfluidic devices can be used to assist in gas evolution monitoring in electrolyzers and batteries, as side reactions may occur in both systems. Li *et al.*[108] examined the effect of flow rate on electrode performance and its correlation with side reactions, such as CO poisoning in fuel cell applications utilizing formic acid. Using a microfluidic chip with multi-microelectrodes array for *in situ* electrode characterization, it was revealed that the anode reaction is likely limited by kinetics (due to CO poisoning) rather than mass transfer, attributed to active sites being blocked by either Pt–CO or bisulphate ions. The results indicated that these challenges can be alleviated through process strategies like increasing the flow rate and oxygen bleeding rather than investing in CO-tolerant catalyst materials such as Pt. These findings are important, as they demonstrate that microfluidic techniques can identify alternative methods for performance optimization other than catalyst material selection.

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Ibrahim *et al.*[24] proposed a microfluidic cell as analytical platform for co-laminar flow cells with dual-pass flow-through electrodes, and explored the impacts of current and flow rate on downstream reactant crossover during discharge operations. Using the proposed dual-pass cell architecture, which can be split into two separate upstream and downstream electrode pairs for individual analysis, they revealed the correlation between operational parameters and crossover losses, providing valuable information for cell optimization strategies. In this method, crossover was calculated based on OCV measurements for both upstream and downstream cell portions, where the difference was attributed to crossover. It was also shown that crossover losses can be reduced by increasing the flow rate, due to reduced residence time in the co-laminar region and diffusive mixing. Yang *et al.*[109] developed a microfluidic device as an analytical platform for zinc–air batteries and Zn-anodes to examine the impact of shear stress and discharge current density on zinc electrode performance (Fig. 6c). In the proposed device, a liquid electrolyte flowed over the zinc-anode and Pt/C cathode simultaneously while the power output was measured. It was shown that increased shear stress, achieved by higher flow rates, improved the power density and cell life due to increased zinc active sites and reduced zinc oxide deposition on the electrode surface. The proposed analytical tool can thus be useful for studying the impact of laminar shear stress and discharging performance of different electrodes, while monitoring cell response based on operating parameters, allowing for enhanced electrode and cell performance.

Microfluidic cells serve as powerful analytical platforms to deepen our understanding of interfacial phenomena governing electrode behavior, including the impact of important considerations such as electrode physical properties (*e.g.*, surface area, wettability, porosity), catalyst deposition methods (*e.g.*, hand painting, air brushing, screen printing), catalyst loading, and catalyst composition. The studies highlighted above reveal how these factors influence electrochemical kinetics, mass transport, and cell performance, including the mitigation of issues such as reaction rate discrepancies, catalyst agglomeration, and electrode flooding. Furthermore, microfluidic systems enable real-time monitoring and in-operando catalyst deposition, offering novel approaches to maximize electrochemical surface area and improve electrode durability. Importantly, insights gained from these microscale investigations can be translated and scaled to optimize electrodes in practical electrochemical devices such as fuel cells, electrolyzers, and batteries. By elucidating interfacial mechanisms and operational parameter effects in controlled microfluidic environments, researchers can design more efficient electrode architectures and fabrication protocols that reduce losses and enhance energy conversion efficiencies in next-generation electrochemical systems.

Cell design. By adjusting factors such as electrode stack configurations and channel dimensions, researchers can systematically explore how these variables affect the performance and efficiency of energy storage systems. For example, different electrode arrangements can be tested to assess their influence on ion transport and reaction rates, while variations in channel dimensions can provide insights into diffusion rates and mass transport resistance within the system. Thus, microfluidics can serve as a powerful tool for enhancing the design and comprehension of innovative energy storage solutions. A variety of cell modification and test condition strategies have been reported in the literature, as summarized in Table 3 and highlighted in Fig. 7.

Channel configuration is a crucial factor to consider for reactant mixing and depletion, significantly impacting the overall system performance. Consequently, various configurations have been discussed in the literature. A Y-shaped microfluidic channel was first proposed by Choban *et al.*[110] consisting of two streams (fuel and oxidant) merging and flowing laminarly in parallel between two coated electrodes without turbulent mixing. This microfluidic cell concept enabled membrane elimination, improved water management, facile product removal, and crossover control. Inspired by this original microfluidic cell design,[110] various other designs have emerged to address mass transport limitations present in the original system, such as the T-shaped microfluidic cell designed by Bazylak *et al.*[111] (Fig. 7a), which aimed to improve fuel utilization while reducing and minimizing fuel-oxidant mixing. Park *et al.*[112] designed and evaluated an H-shaped channel configuration that intended to reduce the size of the mixing region and enhance fuel utilization. The proposed H-shaped cell exhibited higher power density compared to rectangular designs with a thin mixing region. García-Cuevas *et al.*[113] designed and compared cylindrical and star-shaped cells to conventional rectangular Y-shaped microfluidic cells. The primary goal was to create a cell that increased the effective cathode area while maintaining the volume-to-length ratio. Preliminary numerical results indicated that fuel utilization can be improved from 42% in conventional Y cells to 89% and 68.2% for the star and cylindrical cells, respectively. A bridge-shaped cell was proposed by Lopez-Montesinos *et al.*,[114] aiming to confine the diffusive liquid–liquid interface away from the electrodes and minimize crossover by reducing the fuel-to-oxidant interfacial contact, improving fuel utilization. Although the peak power density and OCV were improved (due to reduced crossover), more work is needed to further minimize cell resistance. A trident-shaped cell design was introduced by Ahmed *et al.*[115] to enhance fuel utilization in micro fuel cells, resulting in a fuel utilization of 51% that could be further improved to 86% by tuning other parameters such as cell length and reaction surface area. The proposed system featured three distinct inlets for anode, cathode, and proton-conducting fluids that were connected by small passages. The main goal of this design was to prevent reactants from reacting with the opposite electrode surfaces so that fuel utilization can be improved.

Electrode configuration is another design parameter studied for performance improvement that can also be applied to commercial and large-scale devices. Kjeang *et al.*[116] presented

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Table 3 Summary of microfluidic cell design strategies and key findings

Design optimization	Type	Strategy	Improvement	Ref.
Channel Configuration	Y-shaped	Creating an efficient microfluidic cell	Pioneered advancements in microfluidic systems	110
	T-shaped	Improving fuel utilization by minimizing fuel-oxidant mixing	Enhanced fuel consumption and reduced mixing limitations	111
	H-shaped	Reducing the mixing region and improving fuel utilization	Showed higher power density compared to rectangular channels	112
	Star-shaped	Increasing the effective cathode area while maintaining volume-to-length ratio	Improved fuel utilization from 42% to 68.2% compared to conventional designs	113
	Cylindrical	Similar goals as the star-shaped design	Achieved utilization improvements, needing experimental validation	113
	Bridge-shaped	Reducing crossover	Improvement in fuel utilization	114
	Trident-shaped	Improving fuel utilization	Achieved 51% fuel utilization with higher current densities	115
Electrode Configuration	Planar	Employing inexpensive and effective porous electrode materials	Higher power output and improved fuel utilization (63% per single pass)	116
	Cylinder Array	Increasing available active surface area	Enhanced reactive surface area, power output, and scalability	117
Flow Operation	Flow-over	Improve mass transfer and optimize aspect ratio channel	Achieved peak power density of 70 mW cm^{-2}	120
	Flow-through	Improve active surface area utilization and mass transport	Higher power density and cell efficiency	121
Test Conditions	Environmental Conditions	Understand the effects of temperature and humidity	Increased temperature improved performance significantly; but no further improvement above 45°C	124
	Viscosity	Identify the impact of fuel viscosity on performance	Viscous fuels increased performance and reduced required flow rates	125
	Flow Rate	Evaluate the impact of reactant flow rates on power density	Maximum power density observed at higher flow rates, reducing mass transport limitations	126
	Fuel/Oxidant Composition	Understand the effect of different oxidants (O_2, air, H_2O_2) and their concentrations on cell performance	Improved power density using dilute oxygen, while air was a viable alternative (performance *vs.* cost viability)	127

the first three-dimensional microfluidic cell architecture with multiple electrodes. They examined and compared the performance of planar and three-dimensional electrode configurations composed of a hexagonal array of graphite rods. Performance results revealed that the three-dimensional cell exhibited an order of magnitude higher power output compared to the planar cell when using similar flow rates. Fuel utilization was also improved to 63% per single pass, which was considerably higher than that of the original, planar cell. Zhang *et al.*[117] studied the application of a cylindrical anode array in an air-breathing microfluidic fuel cell with both acidic and alkaline media. The cylindrical anode was proposed because it provides spatially distributed circumferential catalyst surface area and increased reactive surface area, as well as enhanced local fuel transport. Thorson *et al.*[118] explored the impact of electrode length on performance in an air-breathing direct methanol microfluidic cell. Their results indicated that decreasing electrode length improves power density and fuel consumption. Moreover, arranging multiple short electrodes in series was suggested for enhancing fuel utilization and improving cell overall performance. Lee *et al.*[119] studied the optimal conditions for fuel utilization and current density in a microfluidic fuel cell by accounting for transport principles. It was shown that fuel consumption increased as both electrode length and gap were reduced. They also proposed the use of multiple small electrodes (nanoelectrodes) in order to maximize current density and fuel utilization.

Flow operation has also been investigated by numerous researchers. Kjeang *et al.*[120] first introduced a flow-over electrode microfluidic cell configuration with porous electrodes featuring high surface area to boost the reaction rates. The proposed microfluidic device achieved a high peak power density and fuel cell utilization. Later, the same authors[121] introduced a microfluidic cell with a flow-through porous electrode design (Fig. 7b) which is capable of strategically combining the benefits of high surface area and convective mass transport within the porous electrode structure. This flow-through design facilitates improved utilization of the active surface area as well as enhanced convective and diffusion transport rates. Compared to the flow-over design, the flow-through design demonstrated higher peak power densities at lower flow rates and drastically enhanced fuel utilization up to 94%. The cell architecture and electrolyte composition were further refined by Goulet *et al.*[102] to achieve a record-breaking power density of 2.01 W cm^{-2} for liquid based electrochemical flow cells.

Microfluidic cells have also been utilized as analytical tools to investigate the influence of test conditions, such as reactant flow and composition, on mass transport improvements, leading to enhanced system efficiency and

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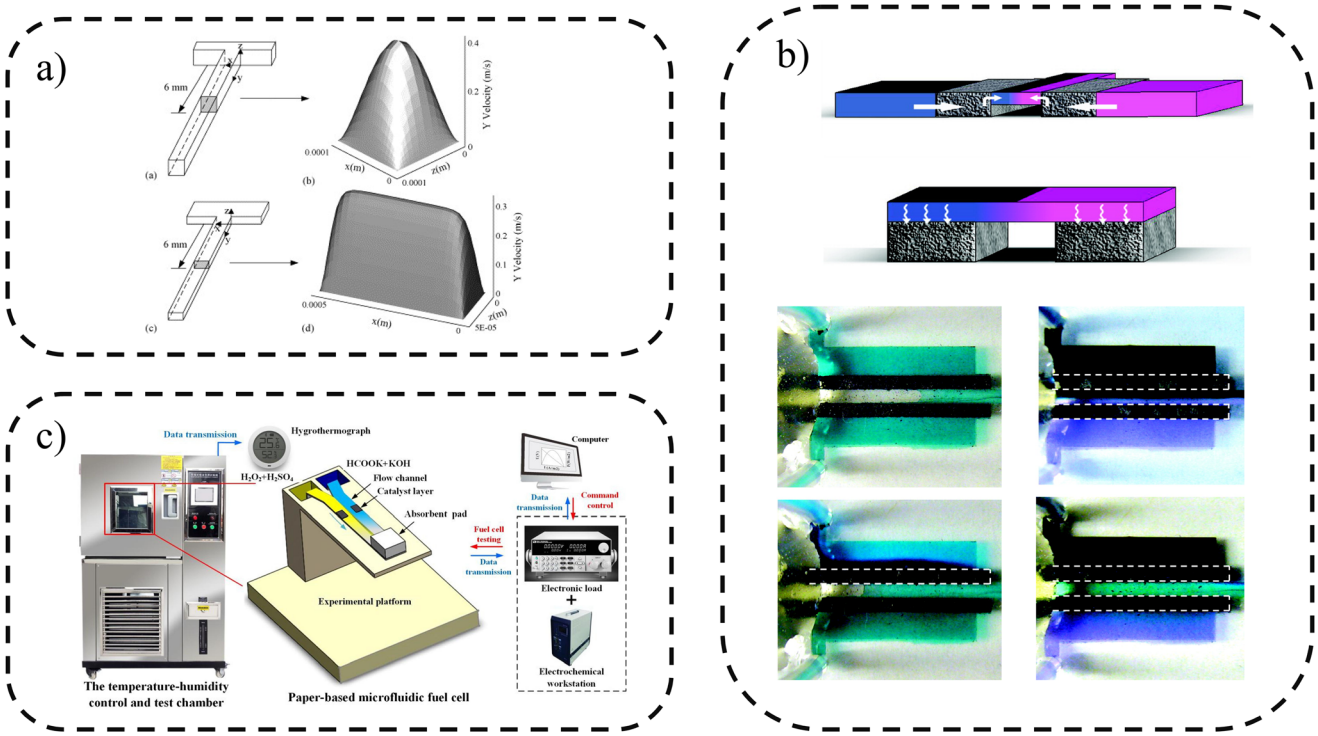

Fig. 7 Cell design and test condition strategies. a) Cross-sectional flow channel geometry. The image is reproduced from ref. 111 with permission from Elsevier, copyright 2005. b) Flow operation (flow-over and flow-through). The image is adapted from ref. 121 with permission from American Chemical Society, copyright 2008. c) Environmental conditions (temperature and humidity). The image is reproduced from ref. 124 with permission from Elsevier, copyright 2023.

reduced fuel consumption. Rathoure and Pramanik[122] employed an air-breathing microfluidic fuel cell to examine the effect of H_2O_2 as a mixed oxidant instead of pure air for methanol electrooxidation. Their results indicated that using H_2O_2 as an oxidant can reduce activation and concentration polarization, allowing power density to increase by supplying additional O_2 to the cathode. These findings are not only beneficial for methanol fuel cells but also for other devices, as it elucidates the impact of different oxidants on overall system performance, which can be adopted for various commercial systems. Kwok *et al.*[123] investigated the performance and fuel utilization efficiency in a solar-assisted methanol microfluidic fuel cell. In the proposed system, hydrogen can be photo-reformed from methanol solution and fed to the microfluidic cell. The microfluidic device consisted of two parts: a fuel tank, which was also the photocatalytic reactor for the hydrogen production, and the co-flow microfluidic cell. Using the same system, they evaluated different methanol to water ratios and its impact on hydrogen production and cell performance. They discovered that an optimal methanol-to-water ratio of 1 : 1 is necessary to enhance power output and fuel utilization, even though hydrogen generation is independent of methanol concentration. These results can be advantageous for *in situ* hydrogen generation and can be applied to both portable and large-scale fuel cell applications. Ma *et al.*[124] explored the influence of environmental conditions on the performance of paper-based microfluidic fuel cells (Fig. 7c). Although relative humidity had a minimal impact on performance at a fixed temperature, the performance improved significantly with increasing temperature from ambient to 45 °C. However, the power density did not increase at higher temperatures (45–65 °C), which can be attributed to the effect of temperature on the catalyst material's catalytic activity. Luo *et al.*[125] examined the impact of fuel viscosity on a methanol microfluidic fuel cell. They conducted performance comparisons between viscous and aqueous fuels, suggesting that adding gelling polymers could increase fuel viscosity and density to mitigate crossover. Performance results indicated that peak power density increased for the proposed viscous co-flow mode of operation compared to the aqueous fuel. By altering fluid viscosity, a lower minimum flow rate was also required. Jayashree *et al.*[126] investigated the performance of a microfluidic hydrogen fuel cell by tuning different operating parameters such as volumetric flow rate, fuel-to-electrolyte flow rate, and oxygen concentration. Their results revealed that maximum power density was achieved at a higher flow rate (50 sccm), attributed to minimized mass transport limitations. At lower flow rates, the cell performance suffered due to low diffusion constants and depletion of hydrogen in the water layer on the anode catalyst layer. Similarly, Déctor *et al.*[127] analyzed the performance of various oxidants (O_2, air, and H_2O_2) at differing formic acid concentrations on a formic acid microfluidic fuel cell. Initially, the effects of

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formic acid concentration were analyzed, revealing performance enhancement as concentration increased from 0.1 to 0.5 M across all three fuel scenarios. However, further increases in concentration had negative effects, primarily attributed to electrode poisoning and slow diffusion caused by the concentration boundary layer. When the compositions of the three fuels were compared, diluted oxygen exhibited the highest power density. Nonetheless, they proposed using air as a more economical and simpler alternative for these devices since its performance was only 22% lower than that of pure O_2. These findings reveal the trade-off between operational and economic factors that need to be taken into consideration in order to optimize the cost-effectiveness of commercial and large-scale applications.

Although much of the knowledge gained from the studies presented in this section—particularly regarding channel configurations and design geometries—is primarily relevant and critical for microfluidic cells, and may not directly translate as scale-up strategies for larger systems, several key insights remain highly valuable for practical, large-scale applications. In particular, the understanding of how operational and test conditions, such as reactant flow rates, oxidant composition, fuel concentration, temperature, and viscosity, influence system performance is essential for optimizing electrochemical devices across scales. For example, the demonstrated effects of oxidant choice on power density and fuel utilization highlight important trade-offs between performance gains and economic feasibility that are universally applicable. It is important to recognize that while channel and cell design approaches must adapt from microscale to macroscale devices due to different flow regimes and mass transport phenomena, fundamental goals—such as maximizing electrode active area, enhancing fuel utilization, improving reactant distribution, and minimizing crossover losses—remain the same. Therefore, microfluidic systems provide a unique and efficient platform to extract critical mechanistic insights and operational parameters, which can inform and guide the design, optimization, and cost–benefit analysis of larger, commercial electrochemical systems.

Modelling and simulation. The simulation of microfluidic systems is a vital tool for advancing energy storage technologies, enabling researchers to predict and analyze the behaviour of fluids and materials at the microscale before developing physical prototypes. By employing computational models, scientists can explore various scenarios and parameter settings, gaining insights into how changes in channel geometry, fluid dynamics, and electrochemical processes can impact overall device performance. The use of microfluidic cells as proof-of-concept tools to validate these models can provide real-world data that assists in refining and calibrating the simulations, ensuring their accuracy and reliability. Combining simulation and experimental validation fosters a deeper understanding of the complex interactions within energy storage devices, facilitating rapid optimization of designs and materials. Furthermore, simulations can identify potential issues and inefficiencies early in the design process, thereby reducing development time and costs. Overall, combining simulations with microfluidic experiments promotes innovative strategies to enhance energy storage technologies, leading to more efficient, durable, and scalable solutions. Some examples on how numerical simulations could be used to optimize cell performance can be seen in Fig. 8.

Bazylak *et al.*[111] examined a computational model for a T-shaped microfluidic cell aimed at improving fuel utilization (Fig. 8a). For that, a computional fluid dynamics (CFD) model was proposed considering coupled flow, species transport, and reaction rates. Fuel utilization results for different geometries were evaluated and compared to experimental data from Choban *et al.* (square geometry)[110] and Ferrigno *et al.* (rectangular geometry).[128] Moreover, the obtained results using the proposed CFD model for the diffusive mixing region width were theoretically predicted with[129] and experimentally validated from Ferrigno *et al.*[128] Simulation results revealed the important role of reactant mass transport and that both inlet velocity and microchannel design significantly influence fuel utilization. They suggested performance optimization by two methods: lowering the inlet velocity and adopting a tapered-electrode design. Krishnamurthy *et al.*[130] developed the first computational model for a flow-through porous electrode microfluidic cell using a numerical multiphysics solver, considering and implementing fluid flow, mass transport, and electrochemical kinetics (Fig. 8b). Several electrochemical metrics were analyzed to understand porous electrode polarization characteristics, including internal mass transport and active surface area, power density, single pass efficiency, and fuel utilization, to determine the optimal device performance based on operating conditions and design modifications. The numerical results, which were validated using experimental data from Kjeang *et al.*,[121] indicated that local concentrations can restrict electrode performance at low to moderate flow rates, while mass transfer and ohmic polarization are the primary limiting factors for high flow rates. Based on the performance of porous electrodes, the authors proposed design changes in electrode and channel geometry to address ohmic resistance and improve the electrolyte flow path. Thus, by combining the proposed computional method from ref. 130 and experimental data from the microfluidic device,[121] this could offer valuable insights for the development and optimization of different electrochemical systems that could benefit from this design tool.

Khabbazi *et al.*[131] investigated the effects of microchannel aspect ratio, electrode configuration, multiple flow streams, and number of inlets on the cell performance metrics of power density and fuel utilization (Fig. 8c). The model integrated fluid flow, charge conservation, mass transport, and reaction kinetics in order to provide polarization curves for the different proposed designs, which were validated using Choban *et al.* experimental data.[110] Their results demonstrated that low aspect ratio geometries are desirable for high current densities, while high aspect ratio geometries perform slightly better at low current densities. It was also shown that system performance can be enhanced by introducing multiple inlets, which can aid in replenishing depleted areas near the electrode–electrolyte

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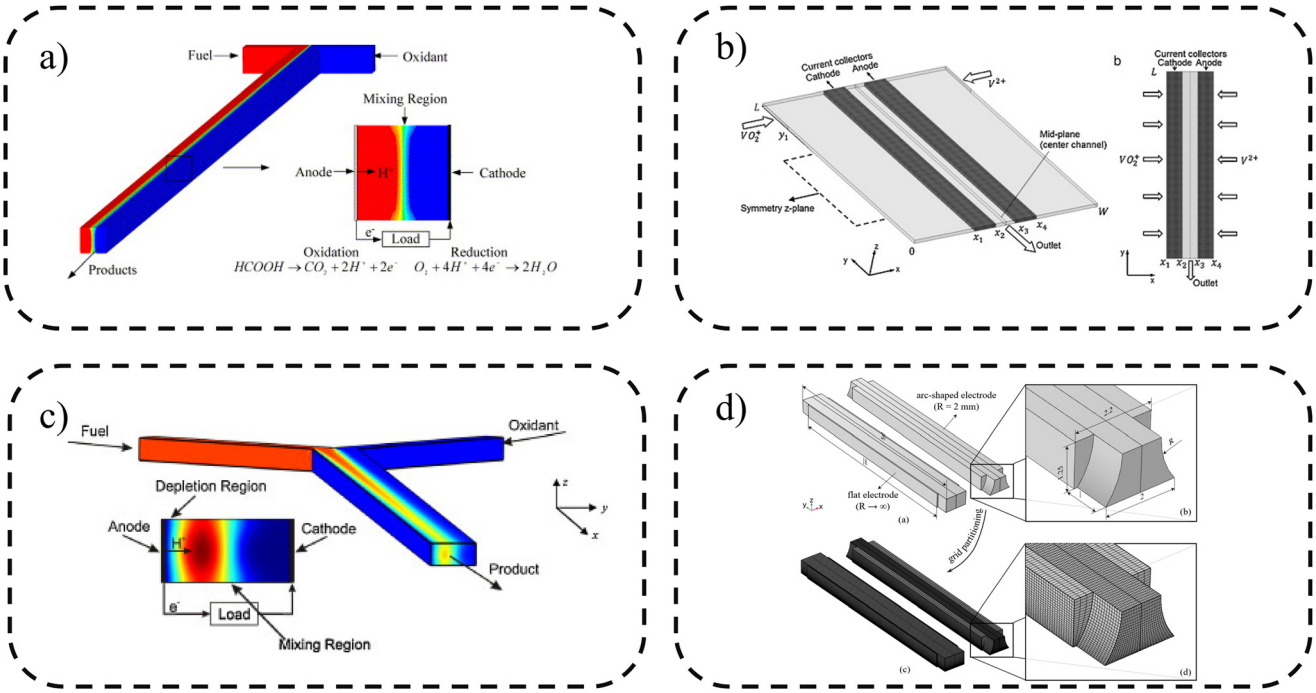

Fig. 8 Computational models used for design optimization of microfluidic electrochemical cells. a) Flow channel dimensions. The image is reproduced from ref. 111 with permission from Elsevier, copyright 2005. b) Electrode arrangement. The image is reproduced from ref. 130 with permission from Elsevier, copyright 2011. c) Channel and electrode geometry. The image is reproduced from ref. 131 with permission from Elsevier, copyright 2010. d) Electrode shape. The image is reproduced from ref. 136 with permission from Elsevier, copyright 2024.

interface. They also proposed a new structural design featuring a tapered channel, which improved fuel utilization fourfold. Marschewski *et al.*[132] examined the effect of mixing promoters on mass transfer rates and performance in membraneless redox flow cells. They combined experimental data using a Y-shaped microfluidix redox flow cell with numerical simulation results. Their findings showed that employing herringbone-inspired flow promoters could substantially enhance mass transfer and alleviate mass transfer limitations by increasing the convection of individual species to the electrodes while minimizing reactant mixing. The numerical model was further combined with experimental data to validate scaling regimes. Wang *et al.*[133] studied the impact of flow configuration on cell performance using a numerical and experimental comparative study, where the numerical method was proposed in order to reveal in-depth mechanisms perceived from experimental data and optimize cell performance economically. Combining both methods, they evaluated the effects of electrolyte flow rate, channel thickness, electrode aspect ratio, electrode distance, electrode area, and outlet design for co-flow and counter-flow cell configurations. The results indicated that counter-flow exhibited lower performance due to uneven current caused by inconsistent ionic resistance across the electrode surface. However, with adjustments to the electrode configuration and cell design (such as electrode distance, electrode area, and outlets), counter-flow cells demonstrated comparable power output to co-flow designs.

Sadeghi and Kjeang[134] proposed a computational model for paper-based microfluidic fuel cells, applied to a novel flow cell design called PowerPAD. For that, they developed a 2-D mathematical model that represented the 3D PowerPAD cell design in order to understand the unique water activated device operation, identify performance limiting factors, and improve its design. These results were analyzed and validated using experimental data from the original PowerPAD cell design reported by Esquivel *et al.*[135] The results indicated that transient back-diffusion and crossover were the primary limitations, and based on cell design modification, they evaluated strategies to improve performance and energy efficiency. By tuning design parameters such as gap distance, electrode width, pad thickness, and pad gap, they managed to achieve a three-fold improvement in cell performance, largely due to crossover mitigation.

Wu *et al.*[136] proposed a new arc-shaped electrode design aimed at adapting to the mixing zone and reducing crossover (Fig. 8d) and built a numerical model in order to evaluate its electrochemical performance. For that, a multiphysics numerical model for an all-vanadium microfluidic cell was developed using governing equations for hydrodynamics, species transport, charge transport, and reaction kinetics. Numerical results provided insights on current density, power density, and fuel utilization, which were validated using experimental data from Kjeang *et al.*[120] The numerical results showed that both power density and fuel utilization were enhanced by improving convective and diffusive mass transport and reducing ohmic resistance. The mechanisms for improved convective and diffisive mass transport were explained by decreased cross-sectional area and compressed

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electrolyte channel, respectively, whereas the ohmic resistance was reduced by shortening the ionic transport path. Dong *et al.*[137] proposed a model for paper-based fuel cells featuring a multiple electrode design. By understanding and encompassing hydrodynamics, mass transfer, and electrochemical reactions kinetics, they developed a new cell design with multiple electrodes and tuned spacing that successfully boosted power output and fuel utilization. By further application of the multi-electrode model,[137] optimization of paper-based microfluidic devices could be achieved.

Overall, this review highlights that integrating numerical modeling with prototyping and experimental testing of innovative microfluidic cell designs constitutes a powerful and cost-effective strategy for advancing electrochemical energy storage and conversion technologies. The studies demonstrate how computational fluid dynamics and multiphysics modeling —addressing fluid flow, species transport, electrochemical kinetics, and charge conservation—can predict key performance metrics such as fuel utilization, power density, and mass transport limitations. These insights enable targeted optimization of cell geometries, electrode configurations, flow parameters, and channel designs to overcome intrinsic limitations like crossover, ohmic resistance, and reactant depletion. Although the majority of the modeling efforts presented are focused specifically on microfluidic cells, the combined approach of modeling and experimental validation remains highly relevant. Microfluidic platforms provide an ideal environment to validate numerical predictions efficiently, facilitating rapid iteration and design refinement. Consequently, the integration of computational modeling with microfluidic experimentation establishes a robust framework that not only advances microscale device design but also provides critical insights and guidance for scaling up and optimizing larger electrochemical systems.

Research opportunities

Microfluidic devices and analytical tools can effectively aid the development of electrochemical energy storage and conversion systems. They have opened numerous opportunities for research and development across various applications. The benefits of applying microfluidics to energy storage and conversion systems include electrochemical characterization, material screening, nanomaterials fabrication, interfacial phenomena characterization, cell design optimization and computational simulations. Although the main contributions and advances in those areas were mentioned throughout this review, there are still tremendous research opportunities that can be addressed by the strategic adoption of microfluidic cells.

For electrochemical characterization, key functional parameters can be extracted from experiments with microfluidic systems. Kinetics and mass transport losses are essential for understanding the system limitations and addressing the factors that hinder performance. Since the early demonstrations of analytical microfluidic cells[120] to the latest designs, the electrochemical characterization of microfluidic systems has yielded improved insights into the properties of electrodes and electrolytes that may not have been fully captured by conventional characterization tools. By applying the knowledge gained from Kjeang *et al.*[120] and Goulet *et al.*,[23] researchers have recognized that dynamic microfluidic systems are crucial for comprehending complex electrochemical reactions. As discussed by Goulet *et al.*,[23] traditional methods could lack accuracy or lead to misinterpretations for porous electrodes or overlook phenomena such as mass transport, which can differ from data obtained under more realistic conditions. Additionally, it is noteworthy that microfluidic cells offer advantages over traditional characterization methods, not only in terms of the sample size and controlled flow inherent to these systems, but also because they can account for various parameters, such as compression and flow rate. Consequently, microfluidic systems can assess the electrochemical processes more realistically, providing greater insight into the performance of electrodes and electrolytes, thus facilitating a deeper understanding of the salient mechanisms and serving as a platform for further improvements. Therefore, new studies could benefit from the use of the proposed microfluidic devices described in the electrochemical characterization section to conduct a **systematic** and **broader** analysis in order to elucidate kinetics and mass transport phenomena and conceive and design new engineering solutions.

As new materials continue to be discovered and proposed, microfluidic systems offer a **fast** and **economical** way to investigate a wider variety of materials with reduced material usage and waste, higher throughput, as well as shorter testing times. New electrode materials, electrolyte compositions and alternative catalyst materials can potentially be evaluated, paving the way for innovative chemistries and formulations. As discussed in the material screening section, microfluidic systems can facilitate the exploration of new catalyst materials that may replace traditional and costly noble metal catalysts utilized in fuel cells, electrolyzers, and other electrochemical systems. Research by Corradini *et al.*[75] demonstrated that prospective catalyst compositions involving rare earth elements can substitute traditional noble metal catalysts commonly found in applications such as direct methanol fuel cells. Additionally, alternative, less expensive, and readily available materials can be examined and implemented in various systems, potentially lowering catalyst costs by offering alternatives to expensive noble metal catalysts. Microfluidic cells can be employed to identify new materials that rival commercial catalyst options, striving for enhanced performance and durability. By minimizing materials usage and waste, microfluidic systems can serve as a greener, more productive platform to expedite catalyst material discovery and development.

The need for fabrication of novel catalyst materials can also be met by microfluidic cells, as these systems can serve as a platform for the production of nanomaterials. By **minimizing** production time, **controlling** shape and size, **simplifying** synthesis and chemical handling, and enabling the synthesis of

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complex and novel structures, microfluidic cells can offer an alternative method for producing nanocatalysts used in electrochemical systems. As demonstrated by Sebastian and Jensen,[99] various metallic and bimetallic nanomaterials can be produced with different compositions and structures. This creates opportunities to explore and fabricate complex structures that traditional methods may not accommodate, or that require intricate fabrication processes involving significant chemical handling and time. Control over nanocatalyst morphology is crucial for applications in electrochemical systems, as it can yield enhanced properties such as electronic conductivity and specific surface area. By adjusting parameters, one can effectively alter the catalyst properties to achieve the desired function. Reducing production time while increasing catalyst yield is vital for catalyst material development, thereby contributing to lower cost.

Interfacial phenomena such as wettability, side reactions, and electrode-catalyst interfaces have a considerable impact on the performance of electrochemical cells, making the **correlation** between physical and electrochemical properties essential for **designing** improved engineering solutions for both electrode materials and electrolyte compositions. Understanding how different properties impact system performance and identifying the main improvement mechanisms is **critical** to tackling these challenges. Therefore, using microfluidic systems as analytical tools can enhance the electrochemical systems by providing a deeper understanding of interfacial phenomena. Microfluidics has proven to be a valuable tool for investigating electrodes in energy storage devices, allowing for precise studies on various energy storage and conversion systems. As discussed by Goulet *et al.*,[23] wettability plays a crucial role in electrode performance, and yet is often overlooked in performance evaluations in the literature. Insufficient information regarding electrode wettability and ECSA can lead to misinterpretations, as improvement mechanisms may be attributed to incorrect reasons, obscuring the true enhancement mechanism. Consequently, understanding the correlation between physico-chemical and electrochemical properties is vital for improving the system performance and concentrating on significant electrode or electrolyte properties that require enhancement. Furthermore, grasping the electrode–electrolyte interface is crucial for catalyst deposition, as also shown by Goulet *et al.*[102] They emphasized that enhancing the wetted ECSA is desirable as it can improve kinetics, thus enhancing electrochemical performance. One approach to achieving this is by enhancing electrode wettability, for which various electrode treatments have been proposed, or by coating catalyst materials with a high specific surface area, as suggested in the literature. However, Goulet *et al.*[102] not only proposed a new methodology for coating catalyst materials in a faster and greener manner but also provided valuable insights into the electrode–electrolyte interface and catalyst attachment. Whether for wettability assessment, catalyst coating, or performance evaluation, microfluidic systems can serve as analytical tools to understand the challenges and mechanisms of interfacial phenomena that can be addressed through novel solutions.

In addition to the development of materials and the discovery of cheaper, more robust, and more efficient alternatives to traditional components such as electrodes and electrolytes, another area of research examines the impact of cell design on system performance. An improved understanding of how electrode dimensions, shape, placement, and reactant and product flows can influence system performance can also be achieved through the use of microfluidic cells. As demonstrated by Kjeang *et al.*,[116] microfluidic cells can **elucidate** the effects of electrode configuration on electrochemical performance, whether utilizing a planar or three-dimensional electrode configuration and flow design, and **their impact** on various parameters such as fuel utilization and crossover. Changes implemented in small-scale devices may potentially be **scaled up** to enhance efficiency in industrial-scale electrochemical systems, which can benefit from the findings and advancements discovered in electrochemical system tests. Besides design, test conditions and durability assessments can also be conducted more rapidly and economically, allowing for the exploration of chemical and mechanical tests for fuel cells, for instance, and a better understanding of the effects of temperature and relative humidity prior to establishing protocols for industrial use. Therefore, microfluidic cells can provide a more rapid evaluation of design parameters and test conditions that are relevant for commercial applications, where time and materials can otherwise restrict the scope.

Lastly, while experimental testing is essential, its high resource intensity may impose a trial and error or empirical approach to finding an optimal condition or, in the catalyst case, an optimal composition among multiple catalyst materials. Such experimental approaches can delay discoveries as multiple variables need to be tested, making the process costly and time-consuming. Therefore, modelling can serve as a **rapid and cost-effective** alternative for testing new designs, discovering new materials, and understanding the impact of various variables in electrochemical systems without the necessity for multiple cell runs. While modelling provides an efficient way to identify improvement strategies for components and the overall performance of the system, it is important to note that data extracted from models often stem from simplified physical representations or may lack essential information, thus resulting in oversimplification and generating results that do not correlate with realistic behaviour. Therefore, microfluidic cells can serve as a **proof-of-concept** platform to validate numerical modelling results, as experimental data are necessary for comparison to ensure that results generated by modelling align with the realities of the system. Experimental data collected by Choban *et al.*[110] and Kjeang *et al.*[121] have been widely employed for validation in various modelling studies, offering valuable insights into how electrochemical systems can be optimized based on different cell modification strategies. Consequently, microfluidic systems can be employed for both experimental evaluations and modelling design, facilitating the development of practical solutions based on the useful information extracted from the data provided by these systems.

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Conclusion

The potential of microfluidic technology as both an analytical tool and a platform for research and development has created new opportunities across many fields, including the electrochemical energy storage and conversion systems covered in this review. The present review highlighted key opportunities and applications of microfluidic cells, illustrating how these devices and tools can address challenges in electrochemical systems, thereby facilitating improved engineering solutions.

Microfluidic cells can evaluate various electrochemical properties, including kinetics and mass transport, as well as assess different electrode materials, electrolyte chemistries, and catalyst materials. These tools have been extensively employed to gain deeper insights into electrode materials and their behaviours under various conditions. Consequently, microfluidics offers a more comprehensive understanding of electrochemical mechanisms compared to traditional techniques, which often overlook crucial characteristics that can impact system performance.

Despite the transformative potential of microfluidics, significant research gaps and opportunities remain that must be addressed to foster innovative solutions. Future advancements in microfluidic technology may lead to new methods for assessing electrochemical performance, screening and discovering novel electrode and catalyst materials, and identifying cell design strategies that could enhance the applicability of microfluidics in the development of electrochemical energy systems.

Thus, the role of microfluidic analytical tools in advancing electrochemical energy storage and conversion technologies is undeniable. As these systems continue to evolve, they will increasingly contribute to the advancement of existing electrochemical systems and conceptualization of new materials and technologies, supporting the development of sustainable energy solutions toward a net-zero emission energy system. The future of microfluidics is indeed promising; it opens avenues for a multitude of research opportunities, paving the way for ground-breaking innovations that will shape the field of energy storage systems and their diverse applications.

Author contributions

C. V. J. S.: conceptualization, investigation, interpretation, and writing – original draft preparation. E. K.: supervision, resources, and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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