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Critical Reviews

Development and status of electrochemical engineering

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ABSTRACT

Electrochemical engineering developed over several decades as the electrochemical industry grew in importance, but was not recognized as an independent, autonomous discipline until Carl Wagner's 1962 paper entitled *The Scope of Electrochemical Engineering* was published. Since then, the discipline of electrochemical engineering has grown greatly, bridging the gap between chemical engineering and electrochemical science. Herein, the contribution is reviewed of electrochemical engineering in the development of electrochemical systems, deployments of which are growing exponentially due to urgent global climate-related challenges of sustainable energy conversion and storage, potable water production and sustainable manufacturing in circular economies. Development and deployment of optimised, efficient electrochemical reactors and processes depend critically on inputs from electrochemical engineering.

Symbol definitions

A_e	electrode area m^2
c_i	electrolyte concentration of species i mol m^{-3}
c_O	concentration of oxidised species mol m^{-3}
c_R	concentration of reduced species mol m^{-3}

Abbreviations: AEM, anion-selective (exchange) membranes; AM, additive manufacturing; BDD, boron-doped diamond; CFD, computational fluid dynamics; CSTR, continuous stirred tank reactor; DES, deep eutectic solvents; DFT, density functional theory; DIET, direct interspecies electron transfer; DNA, deoxyribonucleic acid; DSA, dimensionally-stable anode; EFC, enzymatic fuel cell; FC, fuel cell; FIB-SEM, focused ion beam scanning electron microscopy; GQD, graphite quantum dots; GDL, gas diffusion layer; GDP, gross domestic product; IDDF, integrated disinfection design framework; ILs, ionic liquids; IMO, international maritime organization; KPI, key performance indicator; LED, low-power electronic devices; MCR, measurement control and regulation; MD, molecular dynamics; MEA, membrane-electrode assembly; MEC, microbial electrolysis cell; MET, microbial electrochemical technology; Me/SC, metal/semiconductor; MFC, microbial fuel cell; MIC, microbially influenced corrosion; MO, microorganism; MPL, microporous layer; NAD, nicotinamide adenine dinucleotide; NADP, nicotinamide adenine dinucleotide phosphate; NASA, National aeronautics and space administration; NM/MM, nano/micromotors; ODC, oxygen depolarized cathode; PCB, printed circuit board; PEDOT, Poly(3,4-ethylenedioxythiophene); PEM, proton-exchange membrane; PV, photovoltaic; PVC, polyvinyl chloride; PRC, People's Republic of China; PTFE, polytetrafluoroethylene; PTL, porous transport layer; R&D, research & development; RFB, redox flow battery; RTD, residence time distribution; SEI, solid electrolyte interface; SOC, state-of-charge; TRL, technology readiness level; TSV, through-silicon via; VRFB, vanadium redox flow battery; WE, water electrolyser/electrolysis.

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d	inter-electrode distance m
D_i	diffusion coefficient of specie i m^2 s^{-1}
e^-	electronic charge, 1.60219 × 10^{-19} C
$\boldsymbol{E}$	electric field ($\nabla\phi$) V m^{-1}
E	electrode potential vs. reference electrode V
$E_e^{\ominus}$	standard electrode potential vs. reference electrode V
$E_{O\,/\,R}$	equilibrium potential vs. reference electrode V
E_r	equilibrium electrode potential vs. reference electrode V
F	Faraday constant, 96485.34 C mol^{-1}
$\Delta_r G^0$	standard Gibbs energy change for reaction kJ mol^{-1}
I	current A
j	current density A m^{-2}
j_L	mass-transport limited current density A m^{-2}
j_0	exchange current density A m^{-2}
$\boldsymbol{J_i}$	material flux density of specie i mol m^{-2} s^{-1}
k_m	mass-transport rate coefficient m s^{-1}
k_B	Boltzmann constant 1.3806504 × 10^{-23} J K^{-1}
K	equilibrium constant 1
M	molar mass g mol^{-1}
N_{Av}	Avogadro's constant, 6.02205 10^{23} mol^{-1}
n	reaction charge number 1
P	partial pressure of gas Pa
q	charge density C m^{-2}
Q	charge C
R	gas constant, 8.31441 J mol^{-1} K^{-1}
R	electrolyte resistance Ohm
t	time s
T	absolute temperature K
μ_i	ionic mobility m^2 V^{-1} s^{-1}
U	cell potential difference V
v	electrolyte velocity m s^{-1}
V	volume m^3
w_i^e	specific electrical energy consumption of species i kW h t_i^{-1}
z_i	number of elementary charges on species i 1
α	transfer coefficient 1
β	Tafel coefficient V^{-1}
δ	Nernst diffusion layer thickness m
ε	voidage 1
ϕ	electrical potential V
ϕ_e	electrostatic potential of electronically-conducting phase V
ϕ_{ionic}	electrostatic potential of ionically-conducting phase V
Φ_i^e	charge yield for production of species / phase i 1
η	overpotential (E - $E_{O/R}$) V
υ	electrolyte kinematic viscosity m^2 s^{-1}
σ	conductivity S m^{-1}
μ	dynamic viscosity of water, 8.95 × 10^{-4} N m^{-2} s
ν_e	electron stoichiometry 1
ρ	density g m^{-3}
∇	$\frac{\partial}{\partial x}+\frac{\partial}{\partial y}+\frac{\partial}{\partial z}$ -
∇^2	$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial^2 z}$ -

1. Introduction

In the mid-19th century, the rapid invention of new synthetic dyes by chemists drove the development of the chemical industry, using mainly stirred tank reactors. Some decades later, the first trials were undertaken to create a new academic education scheme combining chemistry with mechanical engineering in UK and USA into chemical engineering courses, based on the concept of unit operations. However, its graduates then were not especially attractive to employers, but this changed at the beginning of the 20th century. The synthesis of ammonia in the Haber-Bosch-Process, first industrialised in 1913, offered completely new challenges of a high pressure, high temperature gas-solid heterogeneous catalytic process, requiring close cooperation between chemists and mechanical engineers; hence, a chemical engineering education became attractive industrially. In many countries at that time, chemical engineering learned societies were founded; *e.g.* American Institute of Chemical Engineers AIChemE (1908), Institution of Chemical Engineers IChemE (1922), and Gesellschaft für Chemische Technik und Biotechnologie DECHEMA (1926).

1.1. Early and present industrial electrochemical processes

In 1865, James Elkington patented a copper electrorefining process with the first plant commissioned in Pembrey, Wales in 1870; the first US plant was built in Newark, New Jersey in 1883. Essentially the same process is still used, producing 23 Mt_{Cu} a^{-1} globally in 2025, as commercial purity copper needs to be > 99.99 % Cu to maximise its electronic conductivity, as required for its main applications in electrical and electronic engineering.

Hamilton Young Castner (1858-1899), a New Yorker, filed a (1892) US patent for NaCl electrolysis with Hg cathodes and graphite anodes to produce Cl_2. then in 1897 Ludwig Mond helped Castner and the Austria chemist, Karl Kellner, to establish the Castner-Kellner Alkali Co., which built chlor-alkali plants throughout Europe.

However, the invention of fluorinated membranes by DuPont in the 1960s enabled membrane electrolysis, now used almost exclusively for chlorine and caustic production with a production capacity of (84 Mt_{Cl2} a^{-1} in 2025) and NaOH (94 Mt_{NaOH} a^{-1} in 2025). The chlor-alkali industry is the basis for approximately 55 % by value of the chemical industry in the EU-27 and EFTA countries; it generated a turnover of almost EUR 770 billion in 2008. The chlor-alkali industry directly employs about 39 000 people, while approximately 2 million jobs are estimated to be directly or indirectly related to the use of chlorine and caustic soda when the numerous downstream activities are taken into consideration [1].

Electrolysis of aqueous zinc chloride solutions for Zn and Cl_2 production was used (1913) in Great Britain and Austria, but in 1915 it was superseded by the presently used aqueous zinc sulfate electrolysis (13.8 Mt_{Zn} a^{-1} in 2025), with the first plants in Montana, USA and British Columbia, Canada.

The Hall–Héroult molten (oxy-fluoride) salt electrolysis process for aluminium production was developed independently by French engineer Paul Héroult and American engineer Charles Martin Hall in 1886; the Bayer process for purification of its alumina feedstock was developed by Austrian chemist Carl Joseph Bayer in 1889. These same processes produced 74 Mt_{Al} a^{-1} in 2025. The EU aluminium industry directly represents a workforce of about 255 000 people and its annual turnover was in the order of EUR 40 billion in 2013 [2].

1.2. Electrochemical engineering

In the mid-20th century, it became increasingly clear that to understand electrochemical processes adequately, especially in their upscaling for industrial deployment, required extension of chemical

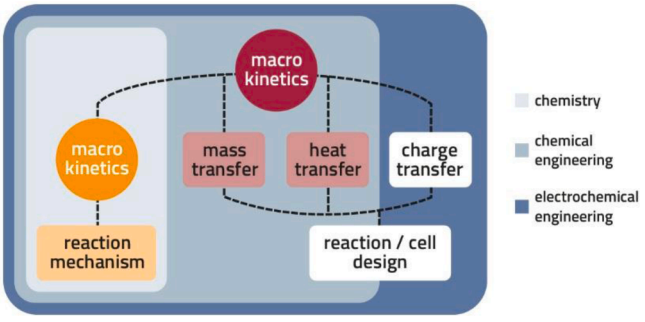


Fig. 1. The scope of chemistry, chemical engineering, and electrochemical engineering.

engineering to include the effects of interfacial charge transfer, leading to the genesis of electrochemical engineering. Fig. 1 shows the scope of chemistry, chemical engineering and electrochemical engineering. Its early pioneers included Carl Wagner, Charles Tobias, John Newman, Fumio Hine and Norbert Ibl. In the subsequent decades, many monographs, seminal publications [3–16], and an encyclopaedia [17] provided a broad overview of the scope of applied electrochemistry and electrochemical engineering.

Carl Wagner [3,4] was the first to apply chemical engineering similarity theory with its dimensionless numbers to the problem of current density distribution at the electrodes of electrochemical cells,

In the 1960s and 1970s, increased environmental awareness also led to numerous new developments in the electrochemical process industries. In chlor-alkali electrolyses, mercury cathodes and 'diaphragm cells' were replaced progressively by reactors incorporating perfluorinated polymeric (Na^+) cation-permeable membranes, originally developed by DuPont for that application [11]. These, together with replacement of graphite anodes with 'dimensionally stable' titanium-based mixed oxide (RuO_2-based) anodes, enabled specific electrical energy consumptions to be decreased greatly, as have oxygen reduction (c.f. hydrogen-evolving) cathodes (Section 3.3.1) deployed industrially recently [18]. Subsequently, those membranes were used in fuel cells and many other electrochemical processes, as were titanium-based anodes.

Various processes for the electrochemical purification of waste water were developed, especially for recovery of heavy metals [19]. New concepts for electrochemical gas purification have also been demonstrated successfully [20]. These developments resulted in electrochemical technologies being established as an important and inseparable part of the chemical industry responsible for providing important chemical commodities and metals. Until 1998, valuable annual reviews on 'Electrolytic Industries'" were published [21] giving production data for the most significant technologies.

In recent decades, the global challenges of the climate crisis, securing safe drinking water (Section 3.2.1), environmental protection (Section 3.2.2), and sustainable development (Section 3.3), have evoked many responses from the electrochemical engineering community. These include more environmentally benign energy conversion and storage by batteries (Section 3.1.1), water electrolysis for hydrogen production [22] and its use in fuel cells (Section 3.1.2), and in general 'power to X' systems (Section 3.1.3).

In 1932, Francis Thomas Bacon developed the first practical alkaline (hydrogen–oxygen) fuel cell, together with electrolyser-fuel cell pairs, generating hydrogen and oxygen gases in electrolysers for subsequent feeding to fuel cells. The patents were licensed to Pratt and Whitney (USA) to enable electrical power generation for NASA space programs since the mid-1960s. Recent rapidly increasing deployment of renewable energy sources in national electrical grids, has caused a resurgence of industrial interest in cyclic electrolyser-fuel cell operations, to decarbonise chemical-to-electrical energy conversion, to provide energy storage (Section 3.1.2) addressing the inherent intermittencies of renewable energy sources, and to better manage grid-scale supply and demand of electrical power.

These topics belong to those most intensively studied according to the number of publications. However, electrochemical engineering definitely is not limited just to these and addresses a broader range of global societal problems, such as cathodic protection of buried metallic infrastructures [23–26], submerged parts of the off-shore oil platforms [27,28], treatment of complex wastes [29,30], electromembrane separation processes [31–33], microreactors design [34] etc.

As follows from the above analysis, electrochemical engineering originally focussed primarily on the topics of mass transport to heterogeneous electrode | electrolyte interfaces and on the local potential and current density distributions. It developed gradually encompassing charge transfer kinetics, fluid dynamics and aspects of materials, such as the technologically important porous or three-dimensional electrodes. Relevant tools were introduced, such as dimensionless criteria, allowing for efficient evaluation of aspects discussed below; presently, mathematical modelling enables efficient analysis of most problems.

The term 'electrochemical process engineering' is sometimes used synonymously with 'electrochemical engineering' in the literature. However, to avoid ambiguity here it is reserved to imply involvement of both electrochemical and non-electrochemical processes, the latter being other unit processes such as separation(s) required in electrosynthesis. Hence, the term electrochemical process engineering potentially implies a wider scope than electrochemical engineering. Conversely, electrochemical reaction engineering implies a narrower scope, as it focusses on electrochemical reactor design alone, to quantify reactor performances in terms of *e.g.* reaction yields, reactant conversions and energy efficiencies.

Despite the significant role of electrochemical engineering in all these developments and innovations, and its formal recognition as a self-standing part of electrochemistry (*e.g.* as a Division 5 of the International Society of Electrochemistry), the wider electrochemical community frequently does not have a clear view of its role and methods used in the transfer of fundamental electrochemical research results into practical application(s). This manuscript aims to provide a synoptic overview of its applications, the tools and methods used by electrochemical engineers and their role in the electrochemical community.

2. Main targets of electrochemical engineering and tools used

Electrochemical engineering encompasses the conception, design, prototyping, performance characterisation, modelling, control and optimisation of electrochemical reactors and processes, drawing on many related disciplines to achieve its objectives. Electrochemical engineering and mainstream chemical engineering share the same theoretical framework, except for those phenomena arising from the distribution of electrical potential (*i.e.* energy per unit charge) in electrochemical systems.

Whereas both electrochemical scientists and engineers analyse components of electrochemical systems using experimental, theoretical and computational methods, in the spectrum with end members electrochemical science and engineering, electrochemical scientists often view such analysis as an end in itself. By contrast, electrochemical (process) engineering may seek to integrate electrochemistry, chemical engineering, chemistry, metallurgy and materials science, membrane science, fluid mechanics, heat and mass transport, electrostatics, physics, electrical engineering, control engineering and electronics. Such wide scope usually necessitates engineers working in teams, often with the ultimate technological objective to conceive designs of reactors and processes, possibly with coupled chemistry and separation processes, for prototyping, performance characterisation, iterative design improvements, up-scaling and optimisation, prior to deployment. As with most chemical processes, simultaneous achievement of adequate energy efficiency, selectivity, economy, durability, scalability and sustainability is required in elegant and environmentally-benign engineered solutions to technological and societal problems.

The number of independent variables in electrochemical reactors and processes usually necessitates numerical modelling, to predict their behaviour for experimental validation, to steer experiments, enable performance comparison between electrode | electrolyte combinations and geometries, facilitate interpretation of results and to optimise cell / reactor design and scale-up. Kinetic and material parameter values from electrochemical kinetic experiments or literature sources may provide inputs for modelling, initially often as lumped parameter models, using those (micro-) kinetic data. These may be extended to finite element models to predict 2D or 3D spatial distributions of potential, reactant and product concentrations and current densities (mass-transport rate coefficients, temperature, *etc.*), ultimately for integration within whole process models. Such distributions may cause non-linearities when up-scaling electrode (and membrane) areas, possibly resulting in spatial

distributions of charge yields, increasing specific electrical energy consumptions and electrode / membrane degradation. Ideally, simultaneous solutions may be required from multiple sets of governing equations to capture interaction effects, *e.g.* of concentration, temperature and fluid flow on current density.

2.1. Specific electrical energy consumptions and costs

Optimisation requires judicious choice of key performance indicators (KPIs) [35], such as charge yield and specific electrical energy consumption, though the sum of capital costs and operating costs need to be minimised by optimising current densities For electrolysis with redox couple (O|R) at an anode (*a*) and redox couple (O'|R') at a cathode (*c*) see equations Eq. (2.1) and Eq. (2.2):

$$O + \nu_e e^- \underset{k_1}{\overset{k_c}{\rightleftharpoons}} R \tag{2.1}$$

$$O' + \nu_e e^- \underset{k_2}{\overset{k_c}{\rightleftharpoons}} R' \tag{2.2}$$

the reactor potential difference is defined in Eq. (2.3):

$$U = -\left(E_{\mathrm{O/R,a}} - E_{\mathrm{O'/R',c}} + \eta_{\mathrm{a,act}} + \eta_{\mathrm{a,transport}} + \left|\eta_{\mathrm{c,act}} + \eta_{\mathrm{c,transport}}\right| + \sum_i \frac{I.d_i}{A_i.\sigma_i}\right) \tag{2.3}$$

has components due to thermodynamic equilibrium electrode potentials (E), activation and transport overpotentials (η) at anode and cathode, and ohmic potential losses due to current I flowing through phase i of conductivity σ_i with path length d_i and cross-sectional area A_i. By convention, the negative sign signifies an anti-spontaneous process. When transport rates are fast in comparison to electron transfer rates so concentration gradients can be neglected, 'activation' overpotentials [36] are often estimated from the Butler-Volmer equation [37,38] or simplifications thereof Eq. (2.4):

$$j = j_0\left[\exp\left\{\frac{\alpha_a F}{RT}\eta\right\} - \exp\left\{-\frac{\alpha_c F}{RT}\eta\right\}\right] \tag{2.4}$$

When the magnitude of either anode or cathode overpotentials are sufficient so the rate of the corresponding reverse reaction can be neglected, taking the first or second bracketed term in Eq. (2.5) results in the approximation for the activation overpotential:

$$\eta_i = \pm RT\Big/(\alpha_i F) ln\left(|j_i|\Big/ j_{0,i}\right) \tag{2.5}$$

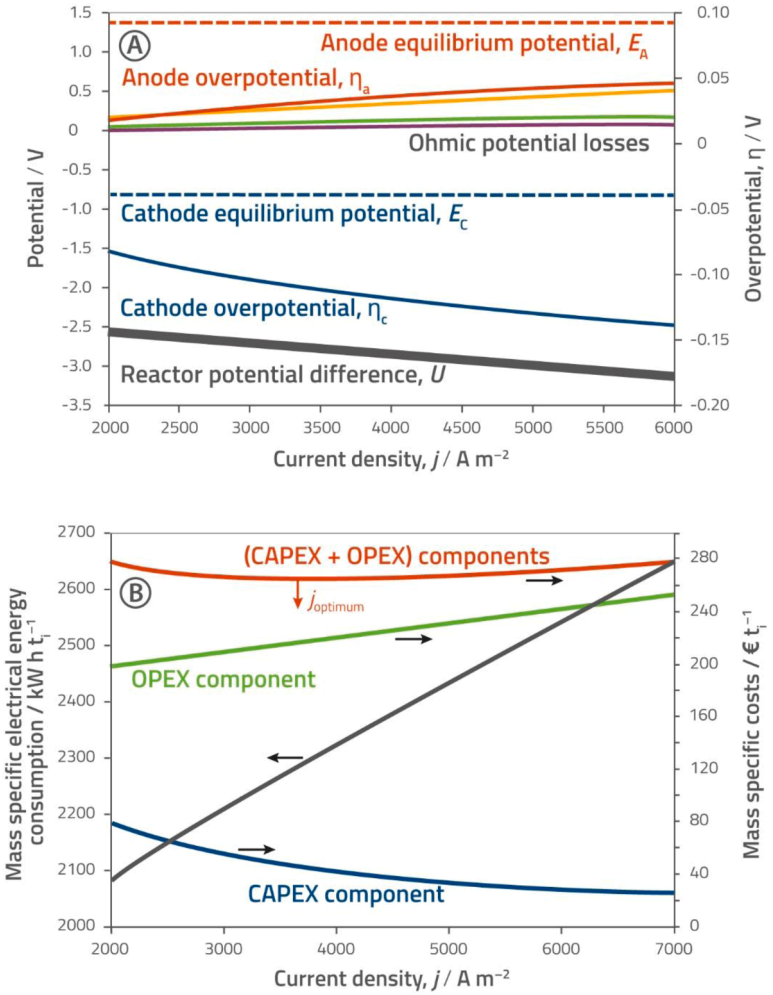


Fig. 2. (A) Effect of current density on contributions to reactor potential difference/voltage, U, (black line) predicted by Eq. (2.3). Red and blue dashed lines correspond to equilibrium electrode potentials at anode and cathode, respectively; operating potential difference (black), cathode overpotential (blue), anode overpotential (red), ohmic potential losses (magenta, green, brown). (B). Schematic effect of current density on specific energy consumption (black), predicted by Eq. (2.6), together with specific operating (opex: green), capital (capex: blue) and total cost components (red). Assumes specific cost of electrical energy 0.1 € (kW h)$^{-1}$.

where j_i represents the (partial) current density (I_i / A_e) for reaction *i*, $j_{0,i}$ the exchange current density, α_i the transfer coefficient and, by convention, signs are positive for oxidations and negative for reductions. For a hypothetical process producing species *i*, with selected parameter values in Eq. (2.3), Fig. 2A shows schematically the effect of current density on the components and their sum to the reactor potential difference between electrodes, *U*. In this particular case, the *U* vs. *j* relationship exhibits approximately ohmic behaviour, as these calculations do not include effects of mass transfer limitations, normally mitigated industrially by dissipating mechanical energy *e.g.* by pumping. If the reaction forming species *i* has an electron stoichiometric factor $\nu_{e,i}$, the specific electrical energy consumption (w_i^e) for electrolytic production of species *i* can be calculated in kW h t_i^{-1} from Eq. (2.6):

$$w_i^e = \left(\frac{\nu_{e,i}F}{\Phi_i^e}\right) \cdot \frac{|U|}{3.6M_i} \tag{2.6}$$

Eq. (2.6) shows the effect of current density, via potential difference *U*, on increasing specific electrical energy consumption for producing species *i*, assuming a charge yield (Φ_i^e) of unity, *i.e.* no parasitic loss reactions, which otherwise would cause a sharp increase in w_i^e, *e.g.* due to mass-transport limitations. When kinetic parameters for the competing reactions are available for the relevant electrode materials and electrolyte compositions, then charge yields can be modelled as a function of electrode potentials. For electrolytic processes, energy costs of specific electrical energy consumptions with pumping costs usually dominate overall running costs. However, for a fixed production rate of species *i*, increasing current densities decrease capital costs (non-linearly), which have to be estimated for each product and process. Hence, as increasing current densities increase running costs but decrease capital costs, the sum of (specific) capital and running costs exhibits, in this case, a shallow minimum with increasing current density, as shown schematically in Fig. 2B.

2.2. Transport processes in electrochemical systems

Homogeneous electronically-conducting (*e*) electrodes in electrochemical reactors obey ohm's law Eq. (2.7):

$$j_e = -\sigma_e \cdot \nabla \phi_e \tag{2.7}$$

where *j* (A m^{-2}) represents the current density vector resulting from gradients in electric potential ϕ_e (V) in electrodes of uniform electronic conductivity, σ_e (S m^{-1}).

In ionically-conducting (*i*) electrolyte solutions involving electrically charged reactant *I* with charge number z_i at concentration c_i (mol m^{-3}), the overall material flux density J_i (mol m^{-2} s^{-1}) to electrode surfaces is due to the three transport mechanisms: migration in an electrical field ($\nabla\phi$), diffusion in an activity / concentration gradient and convection with velocity vector **v**. These flux densities may be approximated by the Nernst-Planck Eq. (2.8), although valid strictly only for ideal (infinitely dilute) solutions in which ion-ion interactions can be neglected, it has been used frequently as a first approximation for the behaviour of more concentrated solutions:

$$J_i \cong -D_i \nabla c_i - u_i c_i \nabla \Phi + \vec{v} c_i \tag{2.8}$$

where the electrical mobility (u_i) of species *i* (*i.e.* velocity per unit electric field strength, m^2 s^{-1} V^{-1}) with diffusion coefficient D_i may be defined by the Nernst-Einstein Eq. (2.9):

$$u_i = \frac{z_i F D_i}{RT} \tag{2.9}$$

Substitution of Eq. (2.8) into Faraday's law (Eq. (2.10)):

$$j_i = z_i F J_i \tag{2.10}$$

enables the material flux density to be transformed into the corresponding current density (Eq. (2.11)):

$$j = F\sum_i z_i J_i = -F\sum_i z_i D_i \nabla c_i - F\sum_i z_i u_i c_i \nabla \varnothing + \vec{v} F \sum_i z_i c_i \tag{2.11}$$

The electroneutrality approximation [39,40] may be applied in well-mixed bulk solution beyond electric double layers at electrodes (Eq. (2.12)).

$$\sum_i z_i c_i = 0 \tag{2.12}$$

This requires the final term ($F\vec{v}\sum_i z_i c_i$) in Eq. (2.11) to be zero, since fluid motion with net zero charge density cannot contribute to net current densities.

In the absence of concentration gradients, *i.e.* for homogeneous electrolytes, $\nabla c_i = 0$, so the penultimate term in Eq. (2.11) is also zero. Hence, Eq. (2.11) simplifies to Eq. (2.13):

$$\mathbf{j}_i = -F\nabla\phi \sum_i z_i u_i c_i \tag{2.13}$$

Which is a statement of ohm's law ($\mathbf{j}_i = -\sigma_i \nabla\phi$) for the conductivity σ_i (S m^{-1}) of (homogeneous) ionically-conducting electrolyte solutions Eq. (2.14):

$$\sigma_i = -F\sum_i z_i u_i c_i \tag{2.14}$$

The prediction implicit in Eq. (2.14) of the magnitude of that conductivities depend linearly on concentrations c_i is a cautionary reminder of the assumption of the Nernst-Planck Eq. (2.8) being limited to idealised solutions in which ion-ion interactions are neglected.

As prediction of steady state behaviour is the focus here, non-faradaic currents due to capacitive (dis)charging of electric double layers at electrode surfaces are not included because of the short time scales involved.

2.3. Spatial distributions of current densities

There are three main (idealised) types of current distributions: primary, secondary and tertiary, each with their own assumptions limiting their applicability, depending on the relative magnitudes of the effects of the different factors affecting those distributions.

2.3.1. Primary current density distributions

At, or sufficiently close to an equilibrium potential ($E_{O/R}$), overpotentials (Eq. (2.4)) are assumed to be negligible, as are concentration gradients in essentially homogeneous ionically-conducting electrolytes with conductivities σ_i, so Ohm's law (Eq. (2.7)) applies.

Potential differences between electronically-conducting (*e*) and ionically-conducting (*ionic*) phases at electrode | electrolyte interfaces are then as in Eq. (2.15):

$$\phi_e - \phi_{ionic} \cong E_{O/R} \tag{2.15}$$

(Primary) current density distributions result from distributions of ohmic potential differences across the electrolyte between electrodes caused by their geometries, *e.g.* higher current densities at electrode edges with current bowing out into electrolyte beyond, or by planar electrode pairs not being parallel to one another.

Despite the limiting assumptions required, predictions of primary current density distributions are useful in providing the most inhomogeneous ('worst case') distributions.

2.3.2. Secondary current density distribution

When the additional resistances ($\partial\eta/\partial j$) corresponding to activation overpotentials (Eq. (2.5)) are coupled to bulk electrolyte resistances, less inhomogeneous potential and current distributions result than in corresponding primary current density distributions.

When a sufficient concentration of supporting electrolyte is present,

thereby decreasing the electric field strength in solution, the migration component of the reactant flux density in the Nernst-Planck Eq. (2.8) is decreased, ultimately to values at which its contribution may be neglected as a first approximation. Then Faraday's law for reaction Eq. (2.1) at current density j_i may be expressed in terms of the reactant's diffusion coefficient D_i and concentration gradient normal (n) to electrode surfaces Eq. (2.16):

$$j_i \cong \pm \nu_e F D_i \frac{\partial c_i}{\partial n} \tag{2.16}$$

Hence, those gradients may be estimated for a range of current densities j_i (and / or as a function of overpotentials estimated from Eq. (2.4)), enabling the range of j_i for which the assumption of absence of those gradients would be an acceptable simplifying approximation. For computational purposes Eq. (2.17):

$$\eta_{O/R} = \phi_e - \phi_{ionic} - E_{O/R} \tag{2.17}$$

2.3.3. Tertiary current density distribution

At sufficiently high local overpotentials for reaction Eq. (2.1), electron transfer rates are predicted *e.g.* by Eq. (2.4) to increase exponentially, causing reactant depletion and product accumulation to occur as mass transport rates become limiting and concentration gradients develop normal to electrode surfaces. This results in concentration overpotentials, η_{conc}, *e.g.* Eq. (2.18) [36].

$$\eta_{conc} = \pm \frac{RT}{\nu_e F} ln \left[\frac{c_{i,x=0}}{c_{i,x=bulk}} \right] \tag{2.18}$$

Hence, the Nernst-Planck Eq. (2.8) for spatial distributions of migration, diffusion and convective flux densities and the corresponding Eq. (2.11) for current density distributions have to be solved, without the simplifying assumptions of primary and secondary current density distributions. This requires iterative solution of coupled partial differential equations for electric potential fields, $\phi_i(x,y,z)$, and concentration fields, $c_i(x,y,z)$, of all ionic and electroactive species, subject to the electroneutrality approximation (Eq. (2.12)) [41]. Those fields are coupled because ionic concentrations affect electrolyte conductivities (Eq. (2.13)) that affect electric potential distributions, which affect migration transport flux densities and potential differences across electrode | electrolyte interfaces that govern electron transfer rates and hence local concentrations. These affect diffusion and convective transport flux densities, local equilibrium potentials, $E_{O/R}$, and concentration-dependent kinetic parameters such as exchange current densities j_0 *e.g.* in Eq. (2.19), depending on how j_0 is defined, *e.g.*:

$$j_0 = F k_0 {c_O}^{(1-\alpha)} {c_R}^{\alpha} \tag{2.19}$$

The (steady state) extended form of the Butler-Volmer Eq. (2.4) includes reactant concentrations at the electrode surface ($x = 0$) and in bulk solution Eq. (2.20) [37,38].

$$j = j_0 \left[\left(\frac{c_{R,x=0}}{c_{R,x=bulk}} \right) \exp\left\{ \frac{\alpha_a F}{RT} \eta \right\} - \left(\frac{c_{O,x=0}}{c_{O,x=bulk}} \right) \exp\left\{ -\frac{\alpha_c F}{RT} \eta \right\} \right] \tag{2.20}$$

Using Nernst's approximation of diffusion layers of thickness δ_N extending from electrode | electrolyte interfaces, surface concentrations at $x = 0$, (*c.f.* well-mixed bulk concentrations ($x = \delta$)) may be estimated from Eq. (2.21):

$$j_i \cong \pm \nu_e F \frac{D_i}{\delta_N} \left(c_{i,x=\delta} - c_{i,x=0} \right) \tag{2.21}$$

In the limiting case when surface concentrations of O or R tend to zero, resulting in transport-limited current densities $j_{L,r}$ or $j_{L,o}$ in Eq. (2.22):

$$j_{L,i} \cong \pm \nu_e F \frac{D_i}{\delta_N} c_{i,x=\delta} \tag{2.22}$$

Substitution of Eq. (2.22) into Eq. (2.21) enables the surface concentrations of O and R to be estimated for any applied current density j_R or j_O relative to their corresponding transport-limited values:

$$\frac{c_{R,x=0}}{c_{R,x=bulk}} = \frac{j_{L,R} - j_R}{j_{L,R}} \tag{2.23}$$

$$\frac{c_{O,x=0}}{c_{O,x=bulk}} = \frac{j_{L,O} - j_O}{j_{L,O}} \tag{2.24}$$

Hence, the concentration overpotential for reduction reaction Eq. (2.1) can be defined by the (concentration-based) Nernst equation and in terms of applied current density relative to its mass transport limited value Eq. (2.18); a corresponding equation can be defined for the oxidation reaction.

Substitution of Eqs. (2.23) and (2.24) into Eq. (2.20) results in a form of the Butler-Volmer equation that allows for transport limitations for both oxidation and reduction of a soluble redox couple O/R by reaction Eq. (2.1), according to Eq. (2.25):

$$j = \frac{j_0 \left[\exp\left\{ \frac{\alpha_a F}{RT} \eta \right\} - \exp\left\{ -\frac{\alpha_c F}{RT} \eta \right\} \right]}{\left[1 + \left(\frac{j_0}{\nu_e F k_{m,R} c_R} \right) \exp\left\{ \frac{\alpha_a F}{RT} \eta \right\} + \left(\frac{j_0}{\nu_e F k_{m,O} c_O} \right) \exp\left\{ -\frac{\alpha_c F}{RT} \eta \right\} \right]} \tag{2.25}$$

Fig. 3 shows examples of the effects of kinetic parameters on the shapes of the resulting polarisation curves for 4 arbitrary chosen values of j_0, defined bulk concentrations of reactants and mass transport coefficients.

In the absence of homogeneous reactions involving species i, a material balance on a differential volume element yields the accumulation or depletion, depending on the net flux density J_i Eq. (2.26):

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i \tag{2.26}$$

Multiplying Eq. (2.26) by $z_i F$ and summing over species i gives Eq. (2.27):

$$\frac{\partial}{\partial t} F \sum_i z_i c_i = -\nabla \cdot F \sum_i z_i J_i \tag{2.27}$$

Substitution of the electroneutrality approximation (2.12) into Eq. (2.27) results in a statement of the conservation of current density or charge Eq. (2.28):

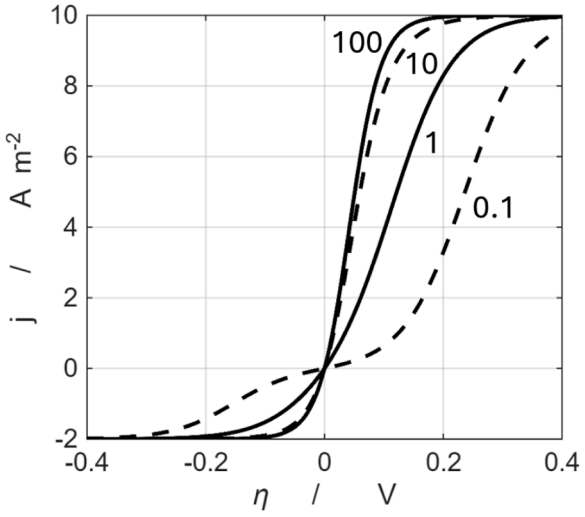


Fig. 3. Polarisation curves for different j_0 (in $[A\ m^{-2}]$ see numbers in the figure). Other input parameters: $\alpha_a = \alpha_c = 0.5$, $k_{m,R} = 1 \times 10^{-4}$ m s^{-1}, $k_{m,O} = 0.2 \times 10^{-4}$ m s^{-1}, $c_O = c_R = 1.0364$ mol m^{-3}, $v_e = 1$, $j_{lim,a} = 10$ A m^{-2}, $j_{lim,c} = -2$ A m^{-2}.

$$\nabla \cdot F\sum_i z_i J_i = \nabla \cdot j = 0 \tag{2.28}$$

Substitution of Eqs. (2.11) into Eq. (2.28) gives Eq. (2.29):

$$F\sum_i z_i \nabla \cdot (D_i \nabla c_i) + \nabla \cdot (\sigma \nabla \phi) = 0 \tag{2.29}$$

Hence, in the absence of concentration gradients ($\nabla c_i = 0$) and for homogeneous electrolytes of conductivity σ, Eq. (2.29) gives Laplace's Eq. (2.30):

$$\nabla^2 \phi = 0 \tag{2.30}$$

Solutions of Eq. (2.30) describe spatial distributions of electrical potential (ϕ) in electrolyte (and electrode) phases.

However, the complexities of the calculations with non-linear boundary conditions imposed by anode and cathode kinetic models, *e.g.* using Eq. (2.5), require numerical solutions of the governing equations, especially for more complex electrode geometries. Such equations may have to be solved simultaneously with sets of other equations, when potentials are dependent on other parameters that are spatially distributed, such as (single- and two-phase [42,43] (bubbly [44])) fluid flow velocities, concentration / composition, temperature *etc*. Solution of local potential and current density distribution models enables design of electrochemical reactors with less inhomogeneous distributions of reaction rates over electrode surfaces, thereby minimising rates of loss reactions and hence minimising specific electrical energy consumptions.

The magnitude of the migration transport flux density contribution to total flux density depends on the presence and concentration of supporting electrolyte, or its absence as in the case of chlor-alkali electrolysis. For example, aqueous H_2SO_4 supporting electrolyte is used in Cu and Zn electrowinning *inter alia* to decrease ohmic potential losses in bulk solution, where the resulting protons carry most of the current density, but their current density across the cathode | electrolyte interface needs to be minimised to maximise charge yields of metal electrodeposition.

Commercially-available software such as COMSOL Multiphysics® in this particular case using the finite-element method, provides 2D and 3D meshing of electrode / reactor geometries, together with in-built equations and databases of material parameters, so greatly facilitating solutions to those 'multi-physics' problems. Effects of electrogenerated bubbles [45] in electrochemical reactors is an example of a phenomenon with multi-scale effects [46] in electrolytic processes of enormous industrial importance: production of hydrogen in water electrolysers, chlorine and hydrogen in (most) chlor-alkali processes, chlorate, aluminium, zinc etc.

However, qualitative predictions of current distributions are possible using a dimensionless group, the Wagner number (*Wa*) [47] as in Eq. (2.31):

$$Wa = \left|\frac{\partial \eta}{\partial j}\right| \frac{\sigma}{l} \tag{2.31}$$

which is defined as the ratio of kinetic polarisation resistance ($\partial\eta / \partial j$) to ohmic resistance per unit area of current path(s) in an electrolyte; larger *Wa* values correspond to less inhomogeneous spatial distributions of current density, whereas a zero value corresponds to the primary current distribution, for which overpotentials are negligible. As implied by this criterion, current density distributions are more uniform for smaller characteristic lengths, larger electrolyte conductivities, and larger gradients of activation overpotential vs. current densities. For kinetically controlled processes, the inverse effect of characteristic length l in Eq. (2.31) implies up-scaling is likely to cause increased distortion of current density distributions, which would be exacerbated by electrodes with increased catalytic performance and hence decreased polarisation resistance ($\partial\eta/\partial j$).

3. Topics presently in the spotlight

This section reviews briefly those topics being studied most intensively by electrochemical engineers at present, merely with an introduction of the main problems and methods.

3.1. Energy conversion and storage

Energy conversion and storage have been one of the most intensively studied topics in developed economies, aiming to decrease their dependences on carbonaceous fossil fuels, using wind, solar and other renewable energy sources coupled to different types of batteries and hydrogen-related technologies to enable sustainable energy systems.

3.1.1. Batteries and redox flow cells

Rapidly increasing deployment of renewable energy systems, based mainly on inherently intermittent wind and solar energies, has recently triggered an exponential growth in the installation of electrical energy / power storage in the order of 10 - 100 MW to balance supply and demand [48,49]. This comprises especially large-scale stationary systems and smaller home-storage systems, but also batteries in electric vehicles. The transition to electromobility is requiring greatly increased national power generation capacities as the chemical energies of fossil fuels are replaced by electrical energy. With suitably incentivised time-dependent tariffs, power utility companies may shift the capital costs of electric grid stabilisation partially to vehicle owners, primarily using Li-ion (and probably Na-ion) batteries with high energy densities and dynamics. For grid-scale applications, also technologies beyond Li-ion batteries may be advantageous, including next generation batteries such as Na-ion batteries and metal-air batteries, and redox flow batteries, which offer facile and less material-intensive scale-up.

3.1.1.1. Li-(Ion) batteries. Li-ion batteries are key components for electromobility, portable and recently also stationary energy storage. Since their first commercialization in 1991, their performances, safety and life-times have increased tremendously, and costs have decreased significantly [50], with electrochemical engineers making multi-scale contributions, experimentally and theoretically to design, production, scale-up, and recently also recycling. Their key analysis and design contribution is the quantification of losses and states of charge inside the batteries and their systematic improvement. For state-of-charge estimation, safe, knowledge-driven operation and experimental deconvolution of the losses in Li-ion batteries, dynamic electrochemical methods like impedance spectroscopy are essential, aided by analysis tools, such as distribution of relaxation times [51] or nonlinear frequency response analysis [52]. Those measurements have been correlated *e.g.* with three-dimensional reconstruction of electrodes from FIB-SEM [53] or tomographic data [54] to visualize and quantify structures, losses and degradation.

Li-ion battery models have been developed by electrochemical engineers, especially by Newman who established porous electrode theory for battery applications [55], used extensively and systematically for Li (-ion) battery analysis, diagnosis and optimization [56,57]. By virtual analysis of battery structures and states, the models yield a better understanding of the processes and losses in batteries. These enable derivation *e.g.* of reaction- vs. diffusion-overpotentials, but also a wide range of additional effects from nm-scale processes like mechanical or chemical surface degradation, *e.g.* particle fracture or solid electrolyte interface (SEI) accumulation, to macroscopic potential and temperature distributions. Examples for such extended models cover SEI growth [58] at nm-scale, or transport through and reaction in microscopic electrode structures [59] or in large cells [60]. The models support identification of strong changes in local conditions that lead to aging or performance losses, and unsafe operation. Models to predict targeted thermal events require thermochemical models with complex reaction networks [61,

62]. Proper identification of battery parameters is a complex but necessary precondition for quantitative insights into processes and losses in batteries and for design and state estimation. For this purpose, engineers developed a complex set of electrochemical and ex-situ parameterisation measurements [63]. The models can also be used for high-throughput screening of cell design and / or cell aging [64,65].

This leads to a further important field of engineering contributions: electrode and battery production and recycling. Engineers employ(ed) and develop(ed) a wide range of production technologies to tune structural and performance parameters of battery components and batteries with low uncertainty. In Germany's academia alone, more than 300 academic researchers are investigating the Li-ion battery production process and the effects of production parameters of the electrodes, but also the effects of electrode cutting and assembling on performance [66]. Experiments with small pilot lines complemented engineers by models at all levels, ranging from single production processes [67], their effects on battery performance including uncertainties [68], to assessing the full production process via combinations of various model approaches with machine learning (see Fig. 4) [69]. The need to balance the huge demand in Li-ion batteries with scarce resources presently triggers rapid growth of research on Li-ion battery recycling [70].

These design, production and analysis methods, both experimentally and model based, are used also for next generation batteries beyond Li-ion technology, such as Li-S, Na-ion or solid-state batteries, that promise increased energy densities and/or decreased costs. Most of these technologies are at an earlier, pre-commercial development stage, at which materials and electrolyte have not yet been fixed. This allows highly effective parallel development and evaluation of the technologies at various levels and intensive interaction of engineers with material scientists, to accelerate the time to market. The different levels of contributions can be exemplified by Li-sulphur batteries. Engineers generated high-energy-density sulphur electrodes using dispersion and calendaring [73]. They identified sulphur reduction kinetics [74] with complex disproportionation reactions from experimentally validated cyclic voltammogram simulations, and elucidated the role of precipitation on performance loss and characteristic discharge behaviour [75] and the role of polysulfide shuttle on the cycling behaviour [76]. Their understanding of the interaction of transport and reaction/precipitation allowed them to identify superior electrolytes to tailor the precipitation of Li_2S [77]. A future vision is that material and battery designers will use virtual engineering tools for optimal design of cells and for virtual optimal operation of this digital twin.

3.1.1.2. Metal-air batteries. Despite the very high theoretical energy densities and potential cost advantages through the use of abundant and inexpensive materials, it has not yet been possible to develop robust and

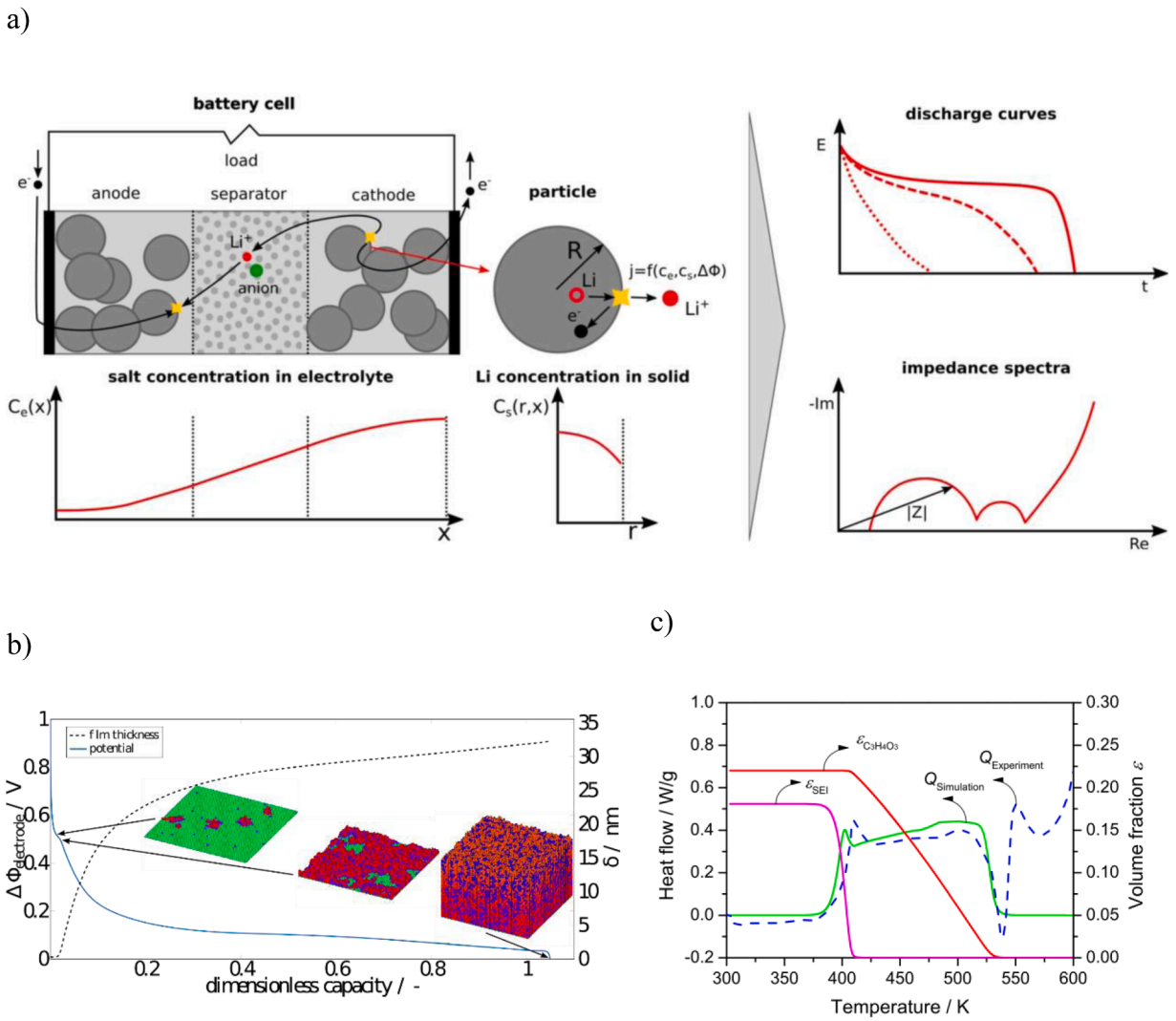


Fig. 4. Battery models cover a wide range of scales and applications using different methods: a) electrochemical models predict battery state and ageing and electrochemical measurements for a given battery/electrode design [57], b) kinetic Monte Carlo models predict inhomogeneous degradation layer formation [71], c) and thermochemical models predict degradation and heat evolution during thermal abuse [72].

technically viable rechargeable metal-air batteries. The most advanced and intensively researched system is the zinc-air battery with alkaline electrolyte and bifunctional oxygen gas-diffusion electrode [78,79]. Electrochemical engineering enabled the development of improved cell components and selection of operational conditions. One example is the application of a flowing electrolyte to mitigate dendrite formation during battery charge and to decrease passivation of zinc surfaces during discharge [80]. For this type of zinc-air cell, a comprehensive multi-physics model was developed, which enables prediction of polarization curves for different operating conditions and to map the limiting current density distribution over the Zn negative electrode during charging [81]. Engineering models also gave valuable insights on the effects of microstructure, cell design [82,83] and the interplay of reactions on Li-air battery performance [84].

3.1.1.3. Redox flow batteries. Since their invention in the 1970s [85], redox flow batteries (RFBs) have attracted growing academic and industrial interest for renewable energy storage, due to their variable scalability of power densities and energy storage capacities. Their broad range of applicable electrolytes [86–90], membranes [91,92], electrode materials and geometries, make them huge fertile areas for scientists and engineers. However, compared to other battery types, RFBs offer relatively low energy densities of about 25 W h kg^{-1}, ultimately due to solubility constraints of electro-active species. Hence, RFBs have been deployed for stationary energy storage applications, with vanadium redox flow batteries (VRFBs) commercialized widely.

Research on VRFBs from components to systems is progressing at multiple scales, as shown schematically in Fig. 5 [93]. It involves increasing energy densities [94,95], improving stabilities of membranes [96–98] and their optimisation by tailoring permeabilities [99] to decrease ohmic potential losses [100] and to decrease crossover rates of negolytes (V^{3+}/V^{2+}) and posolytes (VO_2^+/VO^{2+}) causing self-discharge [101,102]. In addition, developments include electrode materials and geometries [103] to improve kinetics [104–106] and transport, as well as stack design and assembly. Fig. 6 shows a schematic sketch of the planar and tubular VRFBs, each with specific advantages and disadvantages; the planar geometry has more facile current collection and is easier to produce, but the tubular geometry enables easier sealing of individual cells. Heat treatment of the carbon felts [107–110], usually employed as VRFB electrodes, improves battery performance; electrode degradation can be monitored by impedance spectroscopy [108, 111–114]. Segmented laboratory cells enable measurement of current density distributions and state of charge mapping [115,116]; they also enable decreased ohmic resistances and increase performances by aiding flow-field design [117–122], thus decreasing pumping energy losses.

Further engineering challenges involved with scale-up and operation of VRFB are associated with *e.g.* sealing, shunt current losses in the manifolds for hydraulic connections in parallel between cells connected electrically in series in bipolar stacks (Fig. 7) [124,125], battery rebalancing and state-of-charge (SOC) monitoring. Construction of sealed stacks [126] with frame elements containing electrodes and membranes welded to each other prevent leakage of electrolyte. Engineering of electrode geometries with extruded tubular electrodes [123,127] also decrease sealing problems and improve power densities.

Since crossover of negolytes and posolytes through membranes as yet cannot be hindered, rebalancing [128–130] of electrolytes has to be carried out to decrease capacity fading of VRFBs. Knowledge of SOC of VRFBs is essential for reliable battery management, so several methods for SOC monitoring have been deployed [130–139].

Multi-scale modelling of processes in VRFBs from single cells [140] to automatic control of full stacks [141,142] from the microscopic fibre levels [143], has enabled improved understanding, leading to increased battery performances and new approaches to the cell and stack design.

An economic assessment [144] of VRFBs considering components, system design and modelling approaches enabled estimation of system costs. Also, the status and perspectives of VRFBs [145] have been compared to other RFB chemistries. Issues concerning the limited vanadium electrolyte availability and costs, as well as corrosivity and adverse environmental effects, could be overcome by development of innovative chemistries, *e.g.* advanced organic electrolytes [146–152].

Challenges of low RFB energy densities in general could be overcome by development and deployment of bifunctional oxygen diffusion electrodes which could double battery energy densities [153–157].

3.1.2. Fuel cells and electrolysers

Over the last decade, energy conversion in fuel cells and water electrolysers has become more mature through intensive development of more accurate modelling of cell operation, and innovation in their designs.

3.1.2.1. Electrochemical engineering of fuel cells and water electrolysers. A number of models of these energy conversion reactors have been published, incorporating the effects of flow phenomena, transport and transfer processes, as well as electrochemical reactions. The various cell components were considered at the sub-millimetre scales of flow patterns of distribution plates, macro- or micro-porous structures of gas diffusion layers, catalyst supports, and ionomeric membranes. Component degradations have been reported [158], crucially for prediction of Pt-based catalyst degradation.

Aside from these contributions relying upon efficient numerical codes and plausible values for the parameters involved, grey-box approaches have been developed, allowing conceptual tools to evaluate the performance or the limits of fuel cells (FCs) or water electrolysers (Wes). For instance, three dimensionless numbers were introduced to characterise fuel cells [159,160]; in addition to the effectiveness factor, defined as the ratio of the actual reaction rate to the intrinsic reaction rate assuming no transport resistance, two derived Thiele moduli were defined, comparing either the rates of oxygen diffusion and reduction, or those related to oxygen reduction and proton transport. Another example involves Damkoehler numbers which compere the intrinsic reaction area to mass transfer rates in cells or at the reaction interfaces [160,161]. In addition, the effects of transference number of protons

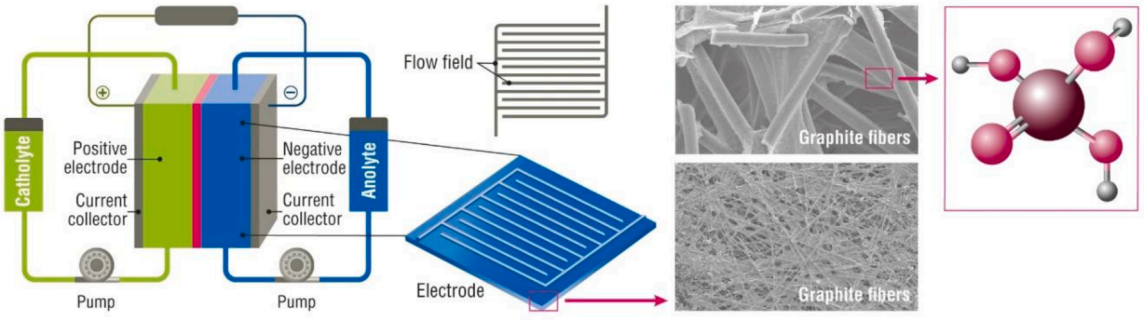


Fig. 5. Engineering of flow cells from stack to molecular level [93].

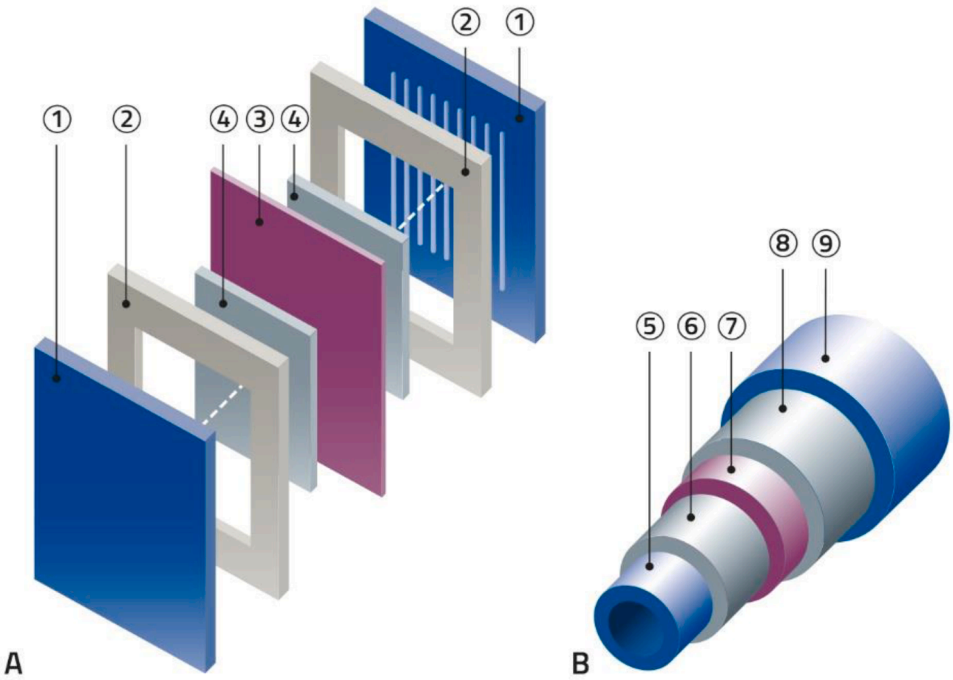


Fig. 6. Schematics of (A) planar flow cell and (B) tubular flow cell [123]. 1 – anode/cathode plate, 2 – flow frames, 3 – ion selective membrane, 4 – porous electrodes, 5 – inner current collector, 6 – porous inner electrode, 7 – tubular membrane, 8 – porous outer electrode, 9 – outer current collector.

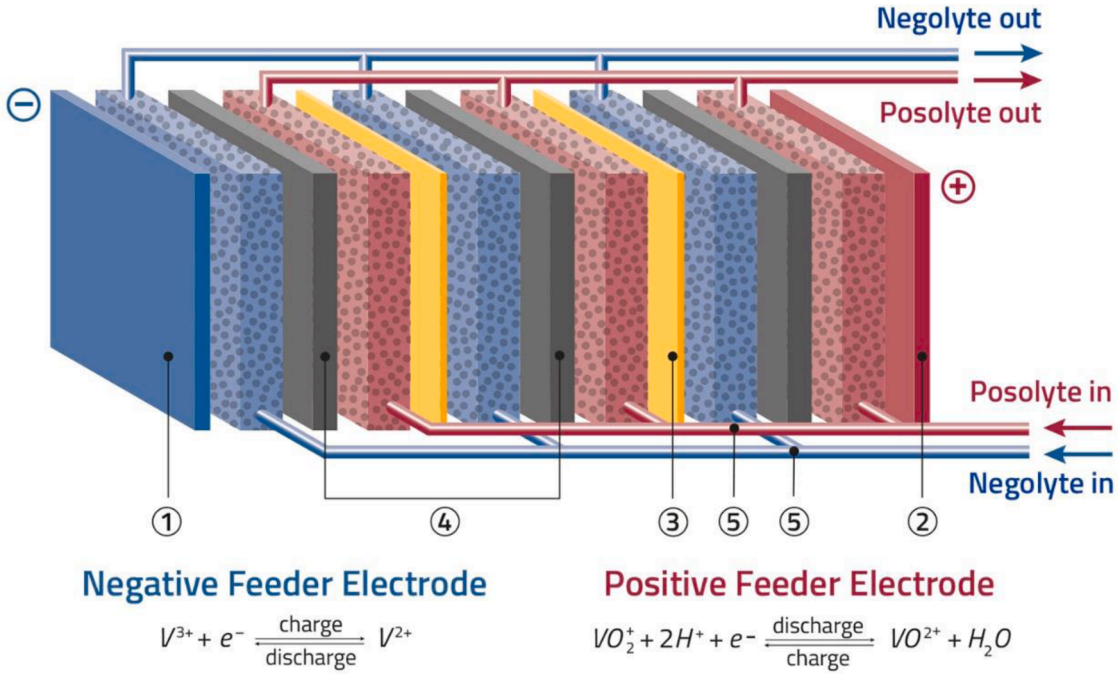


Fig. 7. Schematic vanadium redox flow battery stack in bipolar arrangement.

were considered in a model [162] of the design of microbial fuel cells, to explain limited current densities in systems with neutral or very low acidity solutions. As complements to extensive modelling, these two examples illustrate that 'back to basics' approaches can still help in investigating or designing fuel cells.

3.1.2.2. Imaging phenomena in fuel cells and water electrolysers. Various types of variables or phenomena have been imaged, exemplified by: (i) flow phenomena from distribution plates to catalyst layers, (ii) current density distributions, (iii) gas-liquid flow in proton-exchange membrane (PEM) WEs.

(i) Gas transport through the gas diffusion layer (GDL) is often expressed as through-plane, *i.e.* perpendicular to the GDL plane, or in-plane transport (along the fibre plane), from one channel of the bipolar plate to neighbouring ones in by-passing flow. Alongside the determination of GDL permeability in dedicated cells [163], the strongly anisotropic structure of GDL renders

necessary more precise investigations, as for instance with the aid of Lattice Boltzmann simulations in the porous media and modelling the GDL as a mesoporous medium comprising fibre bundles [164]. The applicability may be questioned of published data of GDL permeability to actual convective gas transport in operating fuel cells, in which transport of hydrogen and air is determined by comparing pressure drops of the gas in the channels, or in through-plane transport, or with flow by-passing over the channel ribs [165]. More recently, equivalent permeabilities of GDLs stacked between two bipolar plates was reported [166] to differ substantially from through-plane or in-plane permeabilities, depending on the presence of a microporous layer (MPL), the flow pattern and the stack clamping torque.

(ii) Current distributions in fuel cells have been shown to be strongly inhomogeneous [167,168], in particular with a large effect of distribution plate flow patterns; aged membrane-electrode assemblies (MEAs) and GDLs were reported to aggravate these distributions [169,170]. In a stack, gas feeding configurations (U-type or Z-type) and the manifold design are additional factors governing gas maldistribution so limiting performances of individual cells. This is why a device for local pressure measurements was successfully coupled to computational fluid dynamics (CFD) modelling and empirical approaches for accurate evaluation of large FC stacks [171]. In closer detail, the shape of stamped channels in metallic bipolar plates also have significant effects on reaction zones under ribs and under channels [172].

(iii) In high temperature solid oxide fuel cells and electrolysers, ionically conducting phases with low conductivities, electronically conducting phases with very high conductivities, and pores forming void fractions are combined judiciously to form composite electrodes, with reactions occurring at 'triple phase boundaries'. Their structural details have crucial effects on spatial distributions of reaction rates and on current collection, so several models have been developed to optimise their properties [173–175].

(iv) In PEM water electrolysers, oxygen bubbles generated at anodes have to flow through porous transport layers (PTL – Fig. 8) before being released in the larger channels of distribution plates. Anode overpotentials depend on gas bubble type for which the wettability of PTL structures and pressures play major roles. Recent modelling involving force and momentum balances, mass balances and electrochemical kinetics [176] were validated by previous experimental data [177] and so can guide improved WE reactor design.

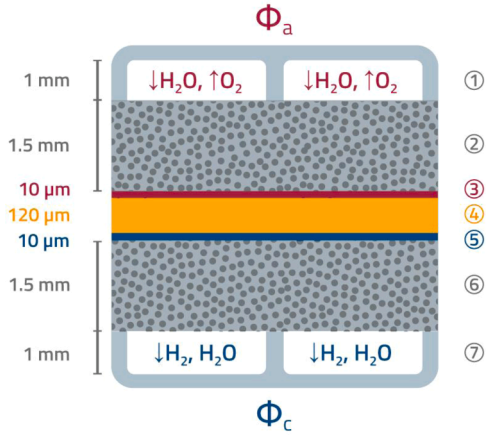


Fig. 8. Schematic of unit cell of bipolar polymer electrolyte membrane (PEM) water electrolyser, with anode potential Φ_a and cathode potential Φ_c. 1 – Ti flow field, 2 – Ti porous transport layer, 3 – anode catalyst layer, 4 – proton conducting membrane, 5 – cathode catalyst layer, 6 – C porous transport layer, 7- Ti flow field.

3.1.2.3. Improved design and performance of fuel cells and water electrolysers. Computational fluid dynamic (CFD) modelling can be developed successfully to improve the design of distribution plates, by favouring under-rib mass transport in PEM cells, for decreasing gas slug flow due to the presence of liquid water and by forcing gas to flow in several successive paths [178]. Less significant gas maldistributions and increased power densities were reported to be achieved by varying the depths of parallel channels in convergent or divergent flow fields, depending on the location of the inlet or gas outlets [179]. These plates tend to have rectangular shapes with horizontal length/width ratios of 2 to 3, and gas channel bends have angles $< 45°$ to limit by-passing over ribs, reduce pressured drop in fuel cells, and so allow more even gas distributions. Combining CFD and neutron radiography for validation of simulation results yielded designs of distribution plates in which hydrogen flows in serpentine channels with long horizontal sections, whereas air is injected downwards and cooling water flows gently downwards [180]. In addition to their flow pattern, the nature of the plate material and its thickness, together with the clamping force, are frequently included in models, using solid mechanical calculations for the sake of more uniform compression inside active parts of cells [181, 182].

Improved water electrolyser designs have enabled more energy efficient cells, with decreased construction costs. For instance, multilayer Ti PTLs with smooth MPL surfaces have been developed with thinner ionomeric membranes, offering increased mass-transport rates and greater access to catalysts [183]. An interesting option relies upon additive manufacturing, allowing efficient and targeted production of fuel cells or electrolysers components. A good example may be industrial inkjet printing able to deposit very low catalyst loadings with gradient distributions [184,185]. Another example is the innovative design of a zero-gap polymer electrolyte membrane alkaline water electrolyser stack, with porous bipolar Ni electrodes, establishing the link between the alkaline water electrolysers and PEMWEs [186]. Finally, non-conductive distribution plates produced by 3D-printing in 'green' polymeric materials such as polylactic acid can be inserted into electrolysers, in which electrical connections are ensured by thin Ti diffusion layers manufactured by wet-etching [187], resulting in decreased manufacturing costs and lower internal contact resistances. In high temperature solid oxide cells, electrodes consist of several layers; that closest to the electrolyte is crucial for electrochemical reaction, while others are responsible for current distribution and gas permeation [188]. Novel 'advanced manufacturing techniques' have enabled 3D printing of ceramic materials for solid oxide electrochemical reactors with specific electrode/solid electrolyte structured interfaces. Cells with corrugated layers showed an increase of 57% in their performances in fuel cell and co-electrolysis (of CO_2 and steam) modes in the temperature range of 800–900°C [189].

3.1.2.4. Microbial and enzymatic fuel cells. In spite of their moderate performances in comparison to PEM fuel cells, biological cells appear attractive as they require no precious metal catalysts, fostering sustained research in life science and engineering for more than a decade. For microbial fuel cells (MFC), as well as for enzymatic fuel cells (EFC), progress made from the life science side are less significant, because the bacteria are usually not inoculated. On the contrary, engineering methods have been used (in addition to the above Oliot's methodological work [162]) to replace the usual batch MFCs with flow systems [190] or to implement control of MFCs from their dynamic analysis [191]. More detailed information is provided in Section 3.5.2.

3.1.2.5. Scaling-up electrolyses and fuel cells. The term 'scaling-up' herein applies to technologies for sustainable energy conversion and

storage beyond the MW scale. To achieve this objective, substantial developments in technical and chemical infrastructures are required, exemplified by a short case study.

Assuming a global gasoline demand of 1 Gt a^{-1} [192] to be met by sustainable alternatives ('e-fuels') alone, with a specific energy required for synthesizing e-fuels [193] from H_2 and CO of 24 MW h t^{-1}, this corresponds to a total energy requirement of 25 PW h. With 1 800 sunny hours a year, the power requirement of 14 TW could be achieved by a total photovoltaic (PV) module area of 68 500 km^2. That figure approximates to present global thermal plus electrical power demands. When constructed over 10 years, this would require installation of 19 km^2 of PVs per day. Detailed calculations can be found in the Supplementary Information. The water electrolysers must be coupled to sustainable energy sources [194] for an effective hydrogen economy [195] based on '*green hydrogen*' [196]. This would require a strict ban of power conversion from fossil oil and coal, otherwise leading to '*red hydrogen*' [192]. The *status quo* of long-term operation (>20 000 h [197]), long system lifetimes (>10-20 years [198]) and high current densities (2.0 A cm^{-2} [197]) need to be increased to > 40 000 h operation and current densities of 3.0–3.5 A cm^{-2}, requiring increased pumping and gas compression rates. Large-scale electrodes require advanced and reliable coating production techniques, decreased area-specific amounts of noble metal catalysts such as Pt and Ir [199], as well as stable and anti-corrosion casings, which should be material-efficient and easily installable.

Use of anion-selective electrolyte membranes (AEM) provide a potential solution to circumvent Ir and Pt scarcity [200,201]. Although much further development is required, AEM-WE has the potential to combine advantages of high current density, dynamic operation of PEM-WE with expanded choice of non-noble metal catalysts offered by alkaline water electrolysis [194,197]. Hence, ongoing R&D activities are occurring in parallel to scaling existing PEM electrolysers [202,203].

During operation, versatility and dynamics of operation are crucial to adapt electrolysers to local needs [204], so should be able to tolerate interruptions as well as partial overloads, while short ramp up and shut down times are desirable. Therefore, in PEM electrolysers, MEAs need to be mechanically, chemically, thermally and oxidatively stable to conditions arising from flexible operational modes [205]. Additionally, a high system availability and low service times are highly desirable, as well as self-sufficiency and independence from supplies and infrastructure [194]. The US Hydrogen Roadmap has a cost target of \$2 $(kg\ H_2)^{-1}$ by 2026 [206].

3.1.2.6. Coupling energy conversion to other processes of interest. Hydrogen oxidation or oxygen reduction can be viewed as convenient reactions at the counter electrode in an electrochemical reactor, for the production of high-value (bio)chemicals, thereby avoiding use or formation of undesired species, and involving proton formation or consumption. Although the energy produced is insignificant, the method was shown to be effective for production of sugar derivatives [207] or regeneration of β-nicotinamide adenine dinucleotide hydrate [208].

Interestingly, energy conversion can be carried out together with water treatment, as done by Tufa et al. [209] who designed an integrated reverse electrodialysis-water electrolysis energy system to decrease the sulphate content of industrial wastewater. Most coupled processes presumably involve microbial fuel cells, in which the waste sludge can be the source of the bacteria allowing energy production [210], or for removal of organic compounds *e.g.* ethanolamine [211], which is largely used in the chemical industry, *e.g.* for CO_2 capture, or in the steam circuits of nuclear plants.

3.1.3. Power-to-X

Although hydrogen production is in general part of this group of processes, it is often referred to separately, as it attracts the largest attention and typically it is an intermediate product in the entire Power-to-X scheme, for conversion of CO_2 to useful molecules by low or high temperature processes.

The low temperature route is typically performed in alkaline environments using gas diffusion cathodes because CO_2 is reduced more efficiently in molecular form than as (hydrogen)carbonate ions [212,213]. The cathode electrocatalyst determines the composition of product mixtures, which are typically formic acid (HCOOH), formaldehyde (H_2CO) and / or methanol (H_3COH) [214]. Unfortunately, the electrical energy input efficiency for this route is thermodynamically limited [215].

The high temperature route is performed typically by CO_2 and steam co-electrolysis in SOECs to produce syngas, *i.e.* equimolar mixture of CO and H_2, at cathodes and oxygen at anodes; then syngas can be used as an input for the Fischer-Tropsch process for more complex molecules, including so called e-fuels (*e.g.* petrol, gasoline, and diesel). Although more extensive reduction of CO_2, ultimately to CH_4 has been reported [216], this is not the desired route of the process as methane is a less valuable product and several undesirable side reactions could occur including 'coking'.

There are numerous engineering challenges connected with the industrial application of the CO_2 reduction, starting with selection of appropriate electrode materials to achieve sufficiently intensive, efficient and selective electrolysis. Competing reactions may lead not only to low Faradaic efficiencies but may cause expensive separation of product from mixtures. Reactors need to be designed and scaled-up to ensure adequate CO_2 transport rates [217] with homogenous CO_2 supply to entire cathode surfaces [218], requiring numerical simulation to validate focused experiments.

3.2. Environmental protection engineering

Environmental technologies are one of the most extensive fields of applications, many of which are focused on removal of anthropogenic species from wastewaters using electrochemical advanced oxidation processes, but also including processes for treating potable water, soil and gaseous effluent streams.

3.2.1. Electrochemical processes for water treatment

Providing safe water for human consumption is one of the main global challenges presently, especially in developing countries, where the lack of water treatment facilities is known to affect public health seriously. In recent years, several electrochemical technologies have demonstrated their capacity to help to overcome this problem, including full-scale electrodialysis for providing potable water to municipalities either from seawater or from brackish inland reservoirs. Electrodeionisation then offers an effective and efficient alternative to ion exchange processes in demineralising water, significantly decreasing chemical demand and enabling continuous processing. Other electrochemical technologies, such as electrocoagulation and electrodisinfection, may displace existing water treatment processes in the near future.

Electro-disinfection is based on electrolytic production of oxidants during the processing of water to remove contained dissolved species, or added on purpose as oxidant precursors such as chloride ions oxidised subsequently to chlorine. However, because of possible formation of chlorinated by-products, production of less hazardous oxidants such as ozone may be preferred.

In addition to disinfection, electrolysis also has been proposed for another important water treatment process: the removal of emerging pollutants, accumulating in natural reservoirs because of discharges of ill-treated municipal and industrial wastewaters, in which concentrations may be very low, *e.g.* endocrine disruptors. Hence, new treatment processes are being developed in which bulk electrolytic processes could be combined effectively with other physical-chemical processes, so that the peculiar characteristics of each of them could be exploited synergistically.

3.2.1.1. Electrocoagulation. Electrocoagulation is an electrolytic technology in which sacrificial electrodes, such as aluminium or iron, are used to promote the formation of coagulant species in treating wastewater or in producing potable water. These species stimulate the aggregation of colloidal particles, *e.g.* silica in raw water into flocs, which can be separated easily from the liquid, either by sedimentation or by flotation. Oxygen and hydrogen bubbles produced, respectively, by the electrolytic oxidation and reduction of water at electrodes produce gentle mixing that enhances the formation of flocs in so-called electroflocculation processes, so minimizing the need for mechanical mixing in treatment processes. In addition, adherence of microbubbles to flocs promotes their flotation (electro-flotation process). The process has been proposed for treatment of industrial wastes [219–222], with many reports of its suitability for water treatment [223,224], for which it is efficient not only for the removal of pollution associated with colloids, including organics and pathogens, but also for removal of ions such as fluorides, nitrates, phosphates and, even, ammonium and arsenic ions [225–231]. This would enable low-quality water to be converted into potable water. Electrocoagulation has been reported to decrease the hardness of water [232], contributing to improving the quality of many water reservoirs. The feasibility of combing this technology with electro-disinfection has been demonstrated recently in the European funded project SAFEWATERAFRICA, providing safe water for rural communities from very low-quality water sources [233–235] with a high content of faecal pollutants. Also, the technology has been reported as suitable for the treatment of hospital wastes [236].

Iron and aluminium electrodes are the most widely adopted, but magnesium [237,238] and zinc [239] have been proposed recently, as demonstrating important advantages in the removal of species such as fluoride ions. The mechanical design of the electrochemical reactors has been reported to affect process efficiencies [240]. The simplicity of the technology, its low specific electrical energy consumption, and outstanding performance explain the great interest in its development. In comparison with chemical coagulation, electrochemically-assisted coagulation exhibits a significant advantage arising from the pH-related changes. While in chemical coagulation, the coagulant agents behave as Lewis acids and tend to decrease the pH of the water to which they are added (often necessitating subsequent neutralisation), electrocoagulation introduces a net reagent in the form of a metal hydroxide. The constituents of this hydroxide (metal ions and hydroxyl ions) are generated at anodes and cathodes, respectively, allowing the amorphous solid to form in solution, causing less pronounced pH changes. In fact, a slight increase in pH is commonly observed in these processes, leading to markedly distinct speciation of the coagulant agents, which translates typically into increased efficiencies in the electrochemical process [228].

3.2.1.2. Electro-disinfection. Many direct and coupled electrochemical technologies have been developed to treat industrial waters, wastewaters and waters in natural environments (ground waters, surface waters, and black waters) contaminated by pathogens. Contaminated waters are disinfected mostly using electrochemical flow cells, the advantages of which compared with the chemical disinfection has been reviewed recently [241]. A larger range of species with high oxidation power may be produced by electrochemical processes, as summarised in the numerous reviews focusing on electrochemical water treatment [242, 243], ballast water [244], water and wastewater [245], electro-oxidation [246], organics [247], electroflotation [248] and nanomaterials [249].

3.2.1.2.1. Inactivation mechanisms. Attached/adsorbed on electrode surfaces, microorganisms (MOs) may be inactivated by direct electron transfer reactions or species produced in the thin reaction layer adjacent to electrode surfaces. At electrode potentials often < 1 V, this method is usually time-consuming, not widespread and not to be confused with electro-adsorption. Though the use of anode materials, such as carbon felt, with high specific surface areas was proposed in early work, the synergistic combination of reduced graphene oxide with boron-doped diamond (BDD) represents a more advanced approach [250]. By extending anode surface areas and decreasing current densities, the selectivity of hydroxyl radical-based reactions can be increased compared to inactivating effects induced by H_2O_2 and ozone, which involve consecutive (electro)chemical reactions with hydroxyl radicals. Electro-adsorption (laboratory and pilot scale) using high-surface activated carbon and carbon cloth electrodes, and the use of electro-deionization cells [251,252], as well as functionalisation of activated carbon electrodes [252,253], can be considered as consistent with development of the described principle.

The second main mechanism is inactivation of MOs by species produced at electrodes and/or in bulk electrolyte solutions, mostly as mixtures of chemicals. Active chlorine species, ozone, H_2O_2, HO_2^- (pH $>$ 11.7), persulfate, chloramines, ClO_2, bromine, different radicals, and others related to these species, depend on pH and other operational parameters. Electroporation could accelerate lethal damage by faster reaction with dissolved disinfectants [254].

Inactivation of MOs in catholyte chambers may also occur by H_2O_2 formed by (partial) oxygen reduction with a gas diffusion cathode [255], inside a flow-through reactor stack with direct anodic oxidation, either at carbon-fibre [256] or modified reticulated vitreous carbon cathodes [257].

3.2.1.2.2. Electrode materials: health risk and efforts for decreasing risk. Many electrode materials (carbon materials, Pt, Pd, titanium activated by IrO_2 and RuO_2, PbO_2, tin oxide-based materials *etc.*) have been deployed in industrial reactors in recent years. However, the development of boron-doped diamond (BBD) electrodes has sparked their use for disinfection [258] leading to reactors available commercially, *e.g.* for producing ozone in halogen-free water, mainly by O_3 gas transfer to systems to be disinfected. However, hydroxyl radicals, and/or ozone have been confirmed to form on BDD anodes, as well as on other materials to lesser extents, forming unwanted by-products, depending on reaction conditions and operational parameters. This is a large problem in drinking water disinfection in which chlorate (ClO_3^-), bromate (BrO_3^-), and perchlorate (ClO_4^-) have to be monitored at mg dm^{-3} concentration levels to avoid health risks [259].

Meanwhile, minimizing or avoiding by-product formation from electrolysis and disinfection by-products from reacting disinfectants with water components such as organic matter, has become a separate research topic [260], in particular when the treated systems are directly health-relevant (drinking water, pool water). Table 1 summarizes results of analysing formation mechanisms and by applying electrochemical engineering principles.

Initially, BDD electrodes were produced exclusively as plate electrodes, so their application was limited by mass-transport rates, though manufacture of three-dimensional BDD foam materials has been reported recently [264,266], though their technical application has yet to be reported. On the other hand, expanded mesh electrodes are available commercially from DIACCON and CONDIAS. To decrease chlorate and perchlorate formation rates, electrode properties [262], shorter residence times [263] and chloramine formation [267] have been suggested.

Inorganic by-product formation rates at relatively low (20 mg dm^{-3}) chloride concentrations have been reported [268] to use the synergetic effects of active chlorine and ozone formation. Aeration of treated wastewater containing bromide ions leads to decreased Br-based by-product concentrations [270]. Formation of chlorate and perchlorate in electrochemical groundwater treatment was reported to be disabled by adding H_2O_2 to the system [271], preventing formation of active chlorine, the chlorate precursor, as demonstrated previously.

In a few countries, inline-drinking water electrolysis for disinfection (unfortunately often named as *Water Activation* or *Anodic Oxidation*) has long been allowed, whereas in other countries it is forbidden, though still researched due to the large variation of reaction conditions, which

Table 1
Engineering activities for lowering halogenate and perhalogenate formation potential on BDD anodes reported 2015–2020.

Strategy	Remarks	Reference
Fine-tune operating conditions	Operation at low current densities and moderate anodic potentials limits the overoxidation of active chlorine species, decreasing the conversion of chloride into chlorate and perchlorate while maintaining sufficient oxidant production for effective disinfection.	[261]
Anode composition optimization	Optimization of the sp^3/sp^2 ratio in BDD coatings modifies the electrocatalytic behaviour of the electrode, favouring the desired oxidation pathways while reducing the formation rates of chlorate and perchlorate by-products	[262]
Decrease residence times	Increasing flow velocity (thus, decreasing hydraulic residence time) reduces the exposure of active chlorine species to highly oxidative conditions, limiting their sequential oxidation towards chlorate and perchlorate.	[263]
3D BDD electrodes	Three-dimensional diamond architectures enhance mass transport and interfacial area, allowing operation at lower local current densities and electrode potentials, thereby improving electrochemical performance while mitigating by-product formation.	[264–266]
Promotion in the formation of chloramines	Controlled generation of chloramines redirects active chlorine speciation away from free chlorine, modifying oxidation pathways and reducing the precursors responsible for chlorate and perchlorate accumulation.	[267]
Operating at low chloride concentrations	Operation under low chloride concentrations exploits the synergistic action of ozone and active chlorine, maintaining disinfection efficiency while suppressing the extensive oxidation sequence leading to chlorate and perchlorate formation.	[268]
Selection of suitable cathodes	The incorporation of carbon felt cathodes promotes the reduction and transformation of oxidizing intermediates, decreasing the net accumulation of undesirable oxychlorinated by-products during electrochemical treatment.	[269]
Aeration	Aeration improves hydrodynamics and modifies oxidant distribution, reducing bromate and other bromine-derived oxidation products formed during the treatment of bromide-containing waters.	[270]
Addition of hydrogen peroxide	Addition of hydrogen peroxide scavenges reactive chlorine intermediates and suppresses active chlorine accumulation, effectively interrupting the reaction pathway that leads to chlorate and perchlorate formation.	[271]

may lead to an uncontrolled matrix of hazardous by-products; standardized salt quality is an additional legal requirement. For small-scale water disinfection, the market is dominated by tubular and parallel plate reactors, with recent designs optimised by mathematical modelling. However, cells divided by diaphragms or ion exchange membranes have been reported in Germany [272].

Wastewaters or toilet waters have to be treated with greatest care, due the extreme risk of inorganic and organic by-product formation. Judicious siting, pre-treatment and novel electrode materials have been recommended for promising results [273].

3.2.1.2.3. Reactor configurations and mathematical models for electro-disinfection cells. The efficiency of disinfection processes is governed by several key factors, including reactor hydrodynamics, but also disinfectant chemistry, and microbial inactivation kinetics. Appropriate reactor design and realistic predictions of reactor performances are then required to obtain the desired disinfection levels. Present approaches for disinfection process design involve application of a $C \times T$ (concentration $\times$ time) Chick-Watson model concept or the integrated disinfection design framework (IDDF) as an overly simplistic description of the disinfection process that can result in operational inefficiencies. Table S1 in the supplementary information lists representative cell types reported.

During water electrolysis with appropriate anode materials, the synergetic effect of electro-generated reactive species, both chlorine- and oxygen-based, and (in a few cases) migrational transport in the electric field close to the electrode surface lead to a highly efficient process for specific organisms that are not susceptible to a single disinfection mechanism [274].

Since most of the conditions required for effective electrochemical disinfection, such as concentration of disinfecting agents and extreme pH conditions, are present only in thin films of electrolyte solutions adjacent to electrode surfaces, so electrochemical reactors should be designed to enable fast transport rates of microorganisms to electrode surfaces. Hence, reactor modelling is a useful tool to design suitable configurations and predict process performance, considering chemical, hydraulic, and biological effects. Residence time distribution (RTD) and CFD analyses must be used in tandem to produce detailed descriptions of reactor hydrodynamics [275], which needs to be combined with mathematical descriptions of the kinetics of production and decay of oxidants.

3.2.1.3. The complexity of research and development. Although many problems in direct electrochemical water disinfection appeared to be solved, development of sophisticated and intelligent technologies

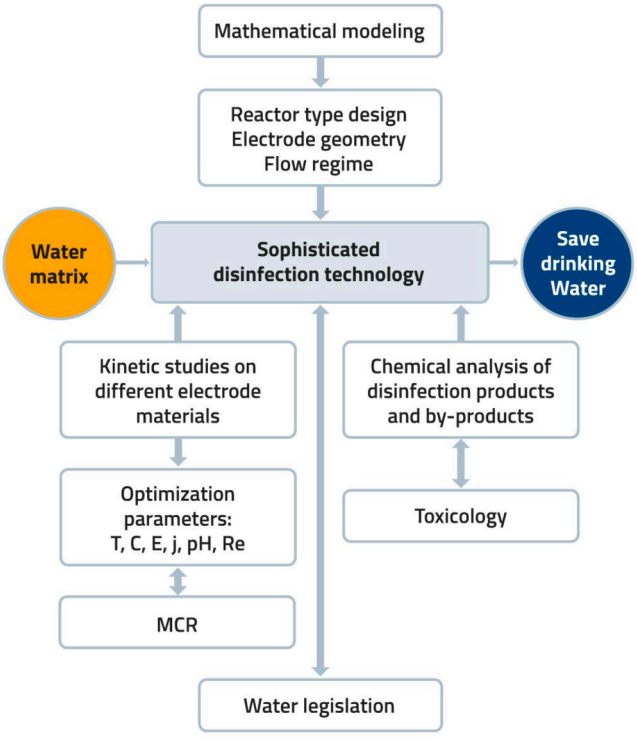


Fig. 9. Scheme of interactions in developing safe electrochemical disinfection technology. MCR stands for measurement control and regulation technology.

remains a highly complex problem. Fig. 9 shows the complex natural science, engineering and legislative interactions necessary for direct electrochemical flow-through drinking water disinfection that is not yet allowed in many countries.

3.2.1.4. New approaches in water treatment. Several new approaches to the reactors system design have attained considerable attention, including reactive membranes. The adaptation of reactive membranes to electrochemical disinfection is a real step forward to novel and innovative technologies, though as yet at the research stage. For example, a titanium sub-oxide anode having filtration properties has been reported [276] and filter-integrated nanowires, which may release silver ions for disinfection have been described [277]; Ag_{28} nanoclusters have been suggested [278] for residual-free disinfection etc.

Another approach represents cells using disinfectant produced in separated reactors to be dosed to the main water stream; divided cells generating concentrated disinfectant liquors have long been known [279].

At mg dm^{-3} concentration levels, undivided cells using tubular and parallel plate electrodes are widespread. As the risk of forming electrolysis by-products may be relatively high at higher current densities, geometrical factors (such as edge effects on electrodes) on current density distributions have been considered [280]. Water quality must be taken into consideration [281]. Chlorine dioxide is another disinfecting and bleaching substance; being unstable, it is produced by chloride electrolysis only at very low concentrations, but is produced industrially 'onsite' by chlorate reduction and chlorite oxidation, normally in the g dm^{-3} concentration range. New chemical and electrochemical technologies for producing ClO_2 at mg dm^{-3} concentrations with charge yields close to 100 % have been reported [282].

3.2.2. Electrochemical processes for wastewater treatment

Improvements in efficiencies of electrochemical advanced oxidation processes are key, as the fundamentals are well established and there is a real need for the applications of these technologies at full-scale, in order to solve important environmental problems [283,284], especially to treat pollutants that are refractory to cheaper technologies. Dilution of these pollutants in wastewaters is one important handicap, as such processes are normally diffusion-controlled with degradation rates fitting first order kinetics. Hence, to achieve a required percentage removal of pollutant, the same electric charge is required, regardless of the initial concentration; *i.e.* to remove 99 % of pollutants of 1000 mg dm^{-3} has the same cost as that to remove the same percentage of a waste containing 100 mg dm^{-3}, although in the first case ten times more pollutant is depleted (990 vs 99 mg dm^{-3}). Hence, preconcentration strategies are a priority.

Examination of the relevant patents highlights two development axes: (i) coupling or hybridization of processes, and (ii) optimised electrode materials, key components of electrochemical processes.

3.2.2.1. Combination or a hybridization of electrochemical processes. As there is no universal treatment process and because the nature of pollutants evolves with society's technological progress, the treatment of effluents will always require innovation to adapt to compositions and volumes to be treated, subject to economic and ecological constraints. Advanced electrochemical oxidation processes producing hydroxyl radicals, the most powerful oxidants in aqueous solutions, are relevant to treatment of bio-refractory compounds, the kinetics of which are limited ultimately by mass-transport rates. To overcome this problem, coupling electrochemical and other processes has been proposed:

(i) chemical processes with coagulation strategies for colloids [285];
(ii) physical processes such as nanofiltration [286], reverse osmosis [287] electrodialysis [288] and absorption [289,290], enabling pollution to be concentrated before electrochemical treatment;
(iii) processes increasing catalytic oxidation rates: ultrasound, chemistry such as Fenton's reaction, photochemistry;
(iv) biological processes; electrochemistry can be used either upstream to reduce COD and toxicity of the effluent or downstream to eliminate bio-refractory compounds [286].

Some processes have reached a sufficient degree of maturity to be available commercially (Table S2 in the supplementary information).

The concept of 'all-in-one' designs or hybrid systems has emerged very recently, integrating various processes, *e.g.*:

(i) Electro-Fenton process cathode and BDD anode for electro-oxidation [291],
(ii) Electrocatalytic membranes: ceramic membranes, usually doped with catalysts and hence conductive [292], so overcoming transport limitations.

3.2.2.2. Electrode materials. As in every electrochemical process, also in water treatment the electrode material plays an important role. In this particular case, electrocatalytic activity and selectivity towards desired electrode reaction is of crucial importance not only because of energy efficiency of the entire process, but also because of sensitivity to the compounds generated, since harmful compounds may be produced in addition to the desired molecules. Therefore, in the following text most important electrode materials used in this field will be discussed briefly.

3.2.2.2.1. Boron doped diamond. Developed at the beginning of the 2000s, boron doped diamond (BDD) electrodes have extraordinary electrochemical properties, enabling many electrochemical applications, such as electrosynthesis, electroanalysis and especially depollution and disinfection, to be revisited [293]. However, its production and operating costs limited its industrialisation and its development to niche sectors. As oxidation using BDD anodes occurs at or in a very thin reaction layer at anode surfaces, mass transport is the main rate limitation. For dilute solutions or as concentrations of target compounds become depleted, most electrical charge is used to oxidize water, so increasing specific electrical energy consumptions exponentially. Therefore, recent BDD development patents over the past few years offer technical solutions by increasing specific electro-active surface areas, including the use of diamond coatings on porous structures (foam, felt) [294–296], diamond powder, and BDD substrates for nanoparticle or nanotube catalysts. To decrease costs and increase electrode strength and durability, various patents have suggested the development of intermediate layers between metal substrates (*e.g.* Nb, Ta) and boron-doped diamond coatings to promote good adhesion of the latter. Such patents have been filed mainly in the People's Republic of China (PRC), whereas hitherto Europe and USA led BDD fabrication. Table S3 in the supplementary information shows the main companies that developed BDD and marketed advanced technology incorporating BDD over twenty years.

3.2.2.2.2. Hybrid/polyfunctional materials. The development of combined processes in turn led to research and possible applications addressing hybrid/polyfunctional materials, micro- or nano-composites, at molecular scales [297,298], the final properties of which are derived not just from the sum of the individual contributions of their components, but also from the strong synergy created by hybrid interfaces [299]. Unique architecture and properties may be achieved to meet the specific requirements of combined processes.

The method used for the synthesis of these structures plays a fundamental role, because it can strongly influence the structure, defectiveness, and the catalytic properties of the resulting material. Among other possible synthetic methods, electrochemical technologies offer the possibility of producing these structures in a controlled manner, with planned morphology and defectiveness which have many applications, both in the field of electro- and photo-electro-catalysis, for biomedical applications, but also in sensors and for the detection and control of environmental pollution.

For example, in photo-electro-catalysis, hierarchical structures with high specific surface areas, consisting of one or more metal oxides, enable increased process efficiencies, exploiting different wavelengths of solar radiation, compatible with the band gap of the various semiconducting materials [300,301]. A recent review [302] examined in detail the top-down and bottom-up techniques dedicated to the synthesis of graphite quantum dots (GQD), highlighting the advantages of the electrochemical oxidation techniques that can be implemented under ambient conditions and do not require complex equipment. They do not involve hazardous reagents/solvents and complex purification and separation procedures and typically take only a few minutes to several hours to produce GQDs with a relatively low number of defects.

The functionalization of surfaces can be carried out effectively with electrochemical techniques, which allow the creation of mono/multilayers compounds that are covalently bonded to the surface [303]. Thus, stable materials, categorizable as *class II hybrid compounds* [304], can be realized with specific terminations that may be useful in selective reactions and exploitable for different specific applications.

In this context, it is worth noting the possibility to functionalize the surface of the so-called nano/micromotors (NM/MM) to make their surface characteristics suitable for effective processes in environmental remediation [305]. It deals with small devices designed to move autonomously in solution, by converting a specific stimulus into mechanical work. Their working mechanism is based on an asymmetry of shape, and/or surface composition, that leads the different areas of the particle to react differently to possible stimuli, determined for example by an external field, whether electric, magnetic, acoustic, or light, but also from a gradient of temperature, or of chemical potential.

Applications of these devices were proposed firstly in the medical and biomedical field for drug delivery: functionalization of surface terminations of these devices can make them selective towards specific molecules, which thus can be captured during the movement of the particles under the action of the stimulus, and released once the stimulus ceases. When the energy derives from a chemical reaction, possible bubbles of gas produced can facilitate the propulsion of the MM, and if its structure is properly designed, the displacement can be consequently directed in a desired direction.

Possible applications in the field of environmental remediation [306] of these devices were first reported at beginning of the past decade [307, 308] devoted to their possible use for the removal of oil from water [309, 310]. Catalytic microtubular Au/Ni/Poly(3,4-ethylenedioxythiophene) (PEDOT)/Pt motors were fabricated by electrodeposition and further functionalized with alkanethiols to form a hydrophobic monolayer on the outer gold surface of the microtube. The strong interactions between the alkanethiol chains and oil from the solution, enable micromotors to capture oil droplets and transport them. MM which exploited the Fenton reaction [311] were also investigated in which H_2O_2 works both as Fenton reactant and fuel to activate the motion of the MM. Depending on the nature of the terminations, the system also can work effectively as sensors for certain molecules to be monitored.

The working mechanism and the reactivity of the devices is strictly linked to the type of environment in which they operate, such as pH, salinity and, above all, to the presence of fuel, generally H_2O_2, which is added to activate the localized production of gas bubbles. Recently, systems that activate propulsion without additional fuel have been reported. The proposed solution is to create NMs based on metal/semiconductor (Me/SC) coupling that can be activated by light radiation, causing electrolysis of the solvent on their surface.

3.2.2.3. Calcareous scaling of cathodes. In electrolyte solutions containing Ca^{II} and Mg^{II} at higher pH, $CaCO_3$ and $MgCO_3$ may be deposited on hydrogen-evolving cathodes, causing as yet unresolved problems in undivided cells. Recently, an interesting cell for wastewater treatment and disinfection was presented [312] having a flexible graphite-polymer composite cathode made from carbon actuated magnetically. The issue is pressing especially in the case of sea water electrolysis. Following the demands of the International Maritime Organization (IMO), ballast water has to be disinfected in modern maritime shipping. Electrochemical cells equipped with BDD and conventional Ti-based DSAs for electro-chlorination are in use at industrial scale [313], but calcareous scaling still remains a challenge, as well as regrowth [314].

3.2.3. Electrochemical processes for soil remediation

Application of electric fields by electrodes placed into soil produces many simultaneous processes, whose extent depends not only on operational parameters, but also on soil characteristics [315]. These processes can be physical (*e.g.* heating), chemical *(e.g.* precipitation), electrochemical (*e.g.* electrolysis of water) or transport processes (electro-osmosis, electro-migration and electrophoresis). With suitable designs, these processes can aid removal of pollutants contained in soil, by dragging contaminants to selected positions from where they can be trapped, extracted, or destroyed [316,317].

For several applications, technology is at a very high technology readiness level (TRL) of 7 to 8, particularly in the case of the removal of metal ion pollutants and volatile species; several companies and governmental agencies are funding full-scale remediation of polluted sites [318,319]. In the first case, technologies applied are based on the promotion of electro-kinetic transport processes, aiming particularly to concentrate and extract metal ions after their electromigration to near electrodes, sometimes combining this transport with metal electrodeposition on cathode surfaces [320,321]. In the second case, the most suitable technology to reach successful application is completely different, as it involves ohmic heating of soil combined with transport of evolved gases for further processing by suitable gas-treatment technology [322,323].

As the application of these two types of technologies has been successful, research on this topic at lower TRLs has been promoted extensively in the last decade at bench and pilot scales [324,325]. In the last decade, this new research has focused not on fundamentals, but mainly on the combination of processes activated by electric fields with efficient non-electrochemical technologies, trying to achieve synergistic combinations to overcome limitations of the non-electrochemical technologies by application of electric fields [326]. Thus, the combination of biological processes with these electrochemical technologies aims to transport nutrients or microorganisms to sites that are difficult to access using pumps [327,328], typically because of low permeability soils, the water content of which also can be modified. In addition, ohmic heating of soils [329] can be used to achieve suitable temperatures for successful bioremediation processes by promoting the metabolism of selected microorganisms. Efficiencies of phytoremediation processes also can be increased by transporting pollutants to near plant roots using electric fields, enabling removal of pollutants contained in greater soil depths [330–332]. The same concept can be applied to abiotic systems, in which electric fields can be used to transport pollutants to permeable reactive barriers, where pollutants can be trapped or modified.

A good example of the first application is the retention of organic pollutants in granular activated carbon beds [333,334], while dechlorination of chlorinated hydrocarbons using zero-valent iron exemplifies the second one, transforming these pollutants into much less hazardous compounds [335,336], which can be depleted biologically. In addition, the use of bio-barriers appears promising, as they enable biological treatment of pollutants in specific sites of polluted soil [337]. Recently, the viability of employing this technology for the remediation of sludge heavily contaminated with organochlorine compounds has been demonstrated in large-scale experimental facilities located at the very site where the contamination was originally contained [338].

This topic is at the interface between electrochemical, chemical and civil engineering; demonstration at TRL4 and 5 of all these technologies opens possibilities of further research with companies aiming to achieve the same applicability in existing commercialized technologies [339].

3.2.4. Electrochemical processes for treatment of gaseous streams

Environmental applications of electrochemical engineering include also treatment of pollutants contained in gaseous streams, in which changes in oxidation state can decrease their danger, or at least minimise environmental impacts of emissions. Electrochemical cells can treat gases directly at gas diffusion electrodes, or alternatively, gases can be absorbed into liquid electrolytes and pumped into electrochemical cells for transformation into less hazardous species, in so-called electro-scrubbing processes. Both alternatives have their advantages and drawbacks as pointed out in a recent report [340].

Many publications have evaluated the treatment of carbon dioxide, sulphur and nitrogen oxides using both electrolytic and, sometimes, fuel cell technologies. Reduction of CO_2 is aimed at producing gaseous (CO, C_2H_4, C_2H_6 *etc.*) or liquid (CH_3OH) fuels or intermediates, which also can be used as building blocks in synthetic processes, when powered by renewable energy for minimizing carbon footprints [341]. For treatment of sulphur and nitrogen oxides, the aim is to transform more hazardous species into less impactful ones [342–345]. As hydrogen sulphide is so toxic and corrosive, its transformation to sulphur, in the so-called electro-Claus process, is important not least for co-production of hydrogen; though conceived in the 1930s [346], apparently it has yet to be deployed industrially.

Possible conceptions of electrochemical air sanitation processes can be classified:

(i) electrochemical preparation of disinfectant solutions and their nebulization;
(ii) passing contaminated air through an electrochemical cell for absorption and disinfection therein;
(iii) production of gaseous disinfectants (ozone, ClO_2, others) and their mixing with a carrier gas (typically air, nitrogen);
(iv) stripping of dissolved disinfectants using a carrier gas;
(v) 'dry' adsorption to high surface area filter or adsorbents with subsequent electrochemical treatment;
(vi) passing air through a liquid in contact with an adsorbent for (electro)adsorption and in situ or successive inactivating of microorganisms;
(vii) combinations with other technologies (*e.g.* photocatalysis [347]).

Method (i) is known from small-scale surface disinfection. Spraying of chlorine solutions for disinfecting subway tunnels was reported recently [348]. Time-stable or onsite produced solutions are necessary for applications. Method (ii) is described in the patent literature [349], but not used in practice. Under the aspects of reaction with surface materials, in [350], a device is presented for mixing ClO_2 with humid air, *i.e.* variant (iii). Commonly, variant (vi) can be found in research as an electro-adsorption method for cleaning contaminated waters. An electrolysing pre-step before electro-spraying and ionization was added to increase disinfection efficiencies [351]. Presently, it can be concluded that despite the potential applications of electrochemical air purification, large scale deployments have yet to occur. Handling of electrolytes, avoiding corrosion effects and corresponding gaseous stream monitoring are the main problems, requiring further research.

3.2.5. Conclusions and future perspectives

Of the technologies evaluated in this section, electrodialysis is clearly at TRL 9 with all elements of the value chain fully developed, commercially available and deployed industrially. Electrocoagulation is at TRLs ca. 6 - 7. However, selected elements of the value chain are still very weak. It is difficult to find providers of technology components, and there are no highly experienced companies offering full-scale commercial installations. The same applies for electro-disinfection, for which there are many companies offering components (electrodes, cells), even applications for swimming pools or spas, but there are some missing elements from the value chain to enable full competition for the direct use of disinfection chemicals.

Electrochemical processes for removal of trace pollutants are at TRL 4 - 5, with many experiments demonstrating removal of pollutants from synthetic and real matrices, but still far from being technically-sound and cost-effective. However, due to anticipated regulatory changes, it is expected to reach commercial levels in the near future.

Regarding this future, a novel concept for wastewater treatment has been proposed recently, in which the ultimate goal is not the remediation of contaminants through mineralisation of the organic matter, but rather their valorisation. This concept is referred to as *electrochemically-assisted organic compound refinery* (or *electro-refinery*), and it is based on the sequencing of three processes: oxidative electrolysis, electrodialysis, and reductive electrolysis [352]. The first stage aims to convert all organic matter into carboxylic acids, leveraging the fact that electrochemical oxidation promotes the formation of oxygenated functional groups and molecular cracking, where the intermediate step prior to full mineralisation into carbon dioxide is the generation of short-chain carboxylic acids. The main challenge in this stage lies in identifying electrocatalytic materials that do not favour complete mineralisation, thereby allowing the accumulation of carboxylic acids. The dissociation of these acids as a function of pH underpins the use of electrodialysis—initially to separate them from the wastewater, and subsequently to purify them. This requires the development of specific anion-exchange membrane technologies, which presently represent a limiting factor. Finally, high-purity carboxylate solutions can be valorised through organic electrosynthesis techniques, transforming carboxylates into alcohols and other organic species. This positions the overall process in alignment with the principles of the circular economy, a situation that becomes particularly evident when the system is powered by renewable energy sources, resulting in a highly sustainable electrochemical waste treatment approach.

3.3. Sustainability in electrochemical production

Sustainability is a major goal of the 21st century to bring human activities and the Earth's ecosystems into balance [353,354], despite 250 years of greenhouse gas emissions causing a significant increase in global temperature [353]. The future sustainable society must be based on a circular economy and resource diversification that is powered exclusively by renewable energies. As solar and wind energies, the most important of these sources to supply electrical energy, a significantly greater importance of electrochemical processes is foreseeable. Kenis [355] has pointed out that various applications of electrochemistry can be associated with sustainability and that the potential role for electrochemical processes to achieve a sustainable world has been evident for decades [356]. Many of these aspects are covered in this review in sections dealing with energy conversion and storage. The present section reviews sustainability in electrochemical production of selected chemical commodities, as well as specialities. Electrochemical manufacturing in the chemical industry has been reviewed briefly [357]. Production of chlorine and aluminium presently are the electrochemical processes operated industrially at the largest scale in terms of tonnes per annum and mass specific electrical energy consumptions, but new opportunities for electrochemical synthesis of organic compounds will arise. For these reasons, chlorine production and the future perspectives of electro-organic synthesis were chosen as examples.

3.3.1. Chlorine production

Chlorine is one of the most important base chemicals, with a global annual production of 84 Mt_{Cl2} a^{-1} in 2025, predicted to grow to 103 Mt_{Cl2} a^{-1} in 2031 [358]. It is used not only for the manufacture of chlorine-containing components (*e.g.*, polyvinyl chloride, PVC), but also is essential for chlorine-free polymers such as polyurethanes and polycarbonates. Chlorine is produced by chlor-alkali electrolysis, in which sodium chloride solutions are electrolyzed to convert chloride ions to elemental chlorine on anodes while sodium hydroxide solution and hydrogen are formed on the cathode, unless oxygen reduction cathodes

are used, now selectively deployed industrially. The more conventional process can be described with the following overall stoichiometry (3.1).

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2 + H_2 \quad (3.1)$$

Since the 1970s, the so-called membrane process has been state-of-the-art in chlor-alkali electrolysis. The invention of perfluoro sulfonic acid ionomers (*e.g.* Nafion^{TM}) in the late 1960s made it possible to separate the two half cells allowing cation transfer from anolyte to catholyte with low electrical resistance, while minimizing transfer of Cl^- ions from anolyte to catholyte, thereby ensuring high caustic purity. Materials development and electrochemical engineering have helped during the continuous improvement of the membrane process through optimization of electrode coatings [359–361], introduction of improved cell designs, namely the zero-gap arrangement with direct placement of the electrodes on the membrane [362], and a better understanding of the complex multiple ion transport across the membrane [363]. This permanent improvement has led to a significant decrease of the specific electrical energy consumption for chlorine production. However, even the most modern plants still need ca. 2 400 kW h t^{-1} Cl_2 [364] with corresponding high carbon dioxide emissions, depending on national fuel mixes. In view of the increasing share of intermittent renewable energy sources, demand-side management, *i.e.* the flexible operation adjustable to the actual energy availability, of energy-intensive chlor--alkali plants has recently attracted great interest [365–368].

Although society is only at the beginning of a hydrogen age, only a fraction of chlor-alkali plants yet make optimal use of the co-product hydrogen. A significant portion is used only thermally through combustion with relatively low energetic benefit, while some plants do not use hydrogen at all [369]. This situation has encouraged the development of new technologies. An obvious possibility is the utilization of hydrogen for electrical energy production in fuel cells. Although demonstrated successfully [370], this route has not been implemented on a larger scale due to limited efficiencies of fuel cells (ca. 50 %, depending on current densities) and the considerable additional investment costs. A more promising way currently represents the avoidance of hydrogen generation through so-called oxygen depolarized cathodes (ODC). ODCs are porous gas-diffusion cathodes in which oxygen is electrochemically reduced to OH^- ions. As the formation of chlorine on the anode remains unchanged, the following overall stoichiometric equation for the ODC process (3.2) is [371]:

$$4NaCl + 2H_2O + O_2 \rightarrow 4NaOH + 2Cl_2 \quad (3.2)$$

Fig. 10 shows a comparison of the cell designs for the standard membrane and the novel ODC process. Compared with the conventional process, the ODC technology decreases the thermodynamic potential difference for chlorine production by 1.23 V (at standard conditions). Given the higher overpotentials for oxygen reduction, the practical benefit is not so great, but decreased cell potential differences of ca. 1 V are possible. Hence, the ODC technology is superior to the alternative uses of hydrogen evolved during chlorine production [372–374].

Key for the successful commercialisation of the ODC electrolysis was the development of properly designed and long-term stable gas diffusion electrodes. As carbon is not sufficiently stable under the harsh conditions (30 wt.% NaOH, 80°C, pure O_2), carbon-free cathodes based on silver as electro-catalysts were developed. The addition of appropriate amounts of polytetrafluoroethylene (PTFE) leads to an optimized hydrophilic-hydrophobic pore structure allowing for intimate contact of oxygen and liquid electrolyte [375,376]. Modelling studies [377–379] have supported the decisive role of a finely distributed electrolyte inside the ODC, because otherwise severe diffusion limitations would lead to increased overpotentials and to low limiting current densities. These predictions were also verified by local measurements of the hydroxide and water activities in the close proximity to the surface of a working ODC [380]. Also, it was shown that the ODC models can be integrated into a model for the full electrolysis cell including temperature effects [381]. Current research is addressing the simulation of electrolyte imbibition in ODCs [382] and operando measurements of electrolyte distributions and transport in ODCs [383,384]. At the systems level, several techno-economic studies on ODC electrolysis [385,386] including the assessment of flexible switching between hydrogen evolving and oxygen consuming operation [387] are available.

Since some of the major products based on chlorine chemistry such as polyurethanes and polycarbonates are chlorine-free, large chlorine-containing waste streams emerge during these synthetic routes. These by-products consist of either chloride salt solutions or of hydrogen chloride. During polycarbonate synthesis, NaCl containing process water is formed, which presently is typically released into rivers. Recycling of these water streams for reuse in the chlor-alkali electrolysis would be an obvious example of production-integrated environmental protection. Covestro already recycles sodium chloride streams at its Uerdingen production site, which started operation in 2015 and is able

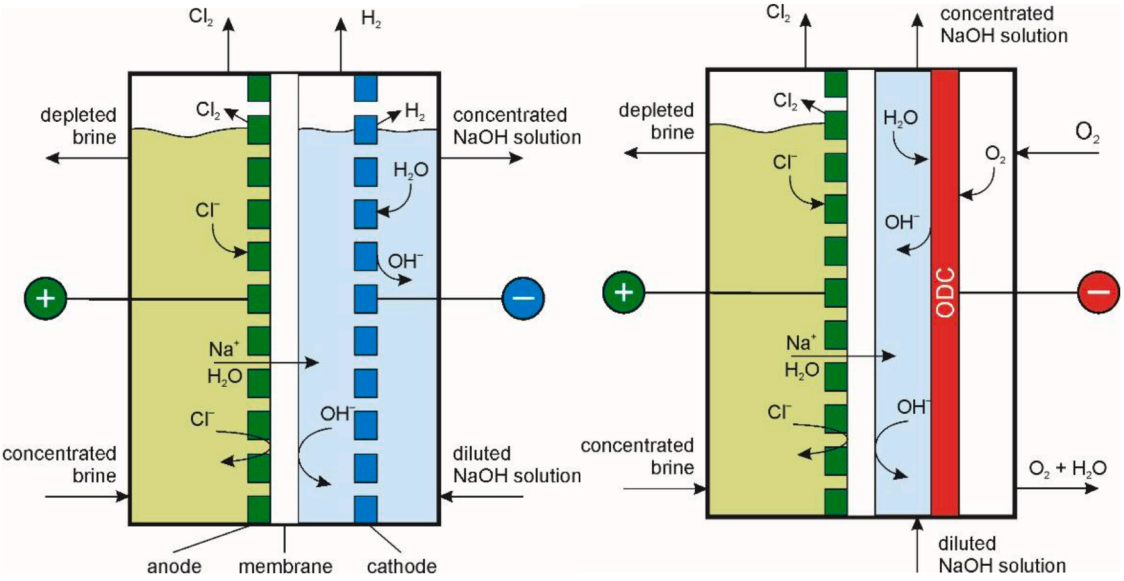


Fig. 10. Comparison of chlor-alkali electrolysis cell with classical hydrogen evolving (left) and oxygen depolarized cathode (right). Reprinted with permission from [371].

to process up to 30 m^3 h^{-1} of salt water, saving 19 kt a^{-1} of NaCl and 2.2×10^5 m^3 of demineralized water [388]. Electrodialysis is a good possibility to concentrate diluted NaCl waste streams [389]. Hydrogen chloride is the main by-product of polyurethane synthesis. For chlorine recycling from HCl, both chemical routes (*i.e.* the different variants of the Deacon process [390]) and electrolysis processes are available. Already in the 1960s, Bayer installed a first plant for chlorine recycling through a classical liquid-phase diaphragm electrolysis. Later, the ODC technology was also introduced for HCl electrolysis. After successful demonstration in a 20 kt a^{-1} plant in 2004, Bayer installed and commissioned a 215 kt a^{-1} plant in 2008 in Caojing, China [391]. Today, liquid-phase ODC electrolysis is the state-of-the-art electrochemical technology for chlorine recycling from HCl. However, energetically even more attractive could be gas-phase HCl electrolysis processes [392], which DuPont patented for electrolytic splitting of HCl into chlorine and hydrogen based on a cation-selective membrane [393]. Remarkably quickly, this new process was demonstrated at a technical scale with a short stack of 2 m^2 cell area operated at a current density of 10 kA m^{-2} and a cell potential difference of 2.0 V [394]. While gaseous chlorine is produced at the anode, hydrogen is evolved at the cathode occurs from recycled dilute aqueous HCl solution, which ensures optimum wetting of the membrane. Preliminary electrochemical engineering models for this process also have been developed [395,396]. Later, the ODC principle was applied also to gas phase HCl electrolysis [397,398]; operating at 4 kA m^{-2} and a cell potential difference below 1.0 V, the specific electrical energy consumption for chlorine recycling decreased to only 733 kW h t $(Cl_2)^{-1}$. Electrochemical engineering helped to further improve this novel process through optimisation of materials [399,400], precise kinetic measurements [401], and the development of advanced models from a single cell (see Fig. 11 for selected results) to the entire recycling process [402–404].

What's next in the chlorine industry? It is clearly foreseeable that chlorine recycling from waste streams will play an increasingly important role in the future. Flexible operation of chlorine producing plant will be necessary for proper integration into the renewable energy system. Given the overwhelmingly important future role of hydrogen as an energy carrier and storage chemical, further expansion of the hydrogen-preventing ODC technology is questionable. An interesting new approach could be the combination of electrolytic chlorine production with carbon dioxide electrolysis to CO, either in separate systems or in a single cell [405]. In this way, the starting materials for phosgene, a necessary intermediate for polyurethane and polycarbonate synthesis, could be obtained using renewable electrical energy alone.

3.3.2. *Organic electrosynthesis*

Electrochemical methods for the synthesis of organic molecules have seen increased use in recent decades across chemistry, materials science, and process engineering [406–408]. Replacing chemical redox reagents – often toxic, metal-derived oxidizing and reducing agents – with electrical energy is a step toward greener processes [409–415]. Organic electrosynthesis offers an alternative route to conventional homogeneous and heterogeneous catalytic processes for producing fine and commodity chemicals. Using electricity instead of hazardous reagents can reduce carbon footprint and waste generation. Furthermore, galvanostatic operation enables safe and dynamic process control, opening opportunities for flexible integration into renewable energy systems.

Although organic electrosynthesis has been researched for more than 100 years [416], particularly since the second half of the 20th century, and despite the fact that more than 80% of industrial products are organic in nature [417], electro-organic processes remain a niche application at the industrial scale [406,413,418–420].

Despite its many advantages, organic electrosynthesis has not yet achieved widespread adoption by process engineers. Consequently, only a limited number of processes have been implemented at the technical or industrial pilot-plant scale. According to literature, less than 30 organic electrosynthetic processes have reached industrial application, with the most prominent examples being the electrochemical synthesis of nylon-6,6 via Monsanto's Baizer process and the anodic methoxylation of p-methoxytoluene to p-anisaldehyde dimethyl acetal developed by BASF (Fig. 12) [421–423]; several additional processes are reported to be in the pilot-development phase [357].

Progress towards technical applications has been limited primarily by the difficulties in minimising mass transport limitations and distributions on scale-up. It is because laboratory-scale development and testing usually occur in single-phase batch reactors with smooth electrode materials and limited specific surface areas [424,425]. Quantitative methodologies for transferring these syntheses to batch or continuous-flow operation remain underdeveloped. Most new organic electrosynthesis reactions are still conducted in batch cells [426–428]; only few employ flow reactors for gram-to-kilogram continuous synthesis [429–432]. At larger scale, single-pass operation is rarely used; recirculating-flow electrolyzers are more common because they support homogeneous concentration profiles and incremental per-pass conversion. In addition to scale-related constraints, electrolyte conductivity in

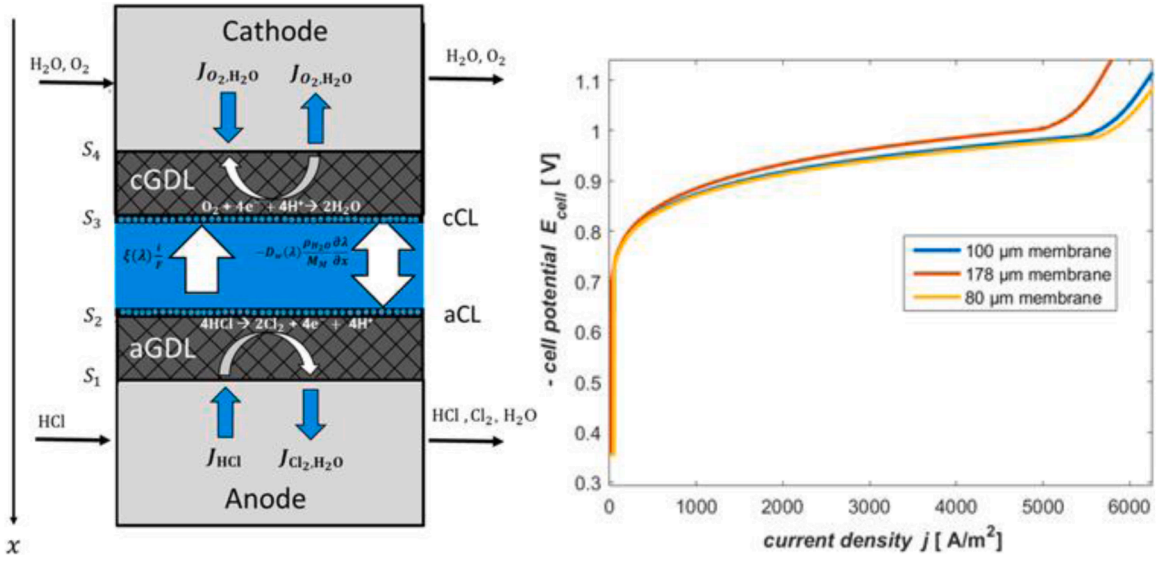


Fig. 11. Modelling domains for HCl electrolysis cell with oxygen depolarized cathode (left) and calculated polarization curves for cells with membranes of different thicknesses. Reprinted with permission from [403].

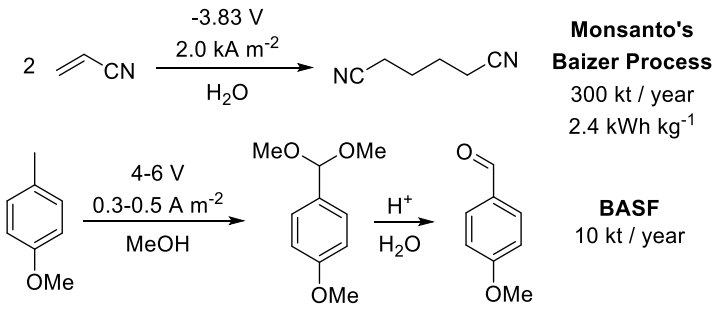


Fig. 12. Electrosynthesis of 6,6-adipodinitrile from acetonitrile (top) and methoxylation of p-methoxytoluene (bottom) [357,422,423].

weakly polar solvents is often limited by poor supporting-electrolyte solubility, leading to high ohmic potential losses. This drives the use of very high electrolyte concentrations or ionic liquids [433,434]. which increases costs and complicates purification, recycling, and waste disposal [412,435]. Solid polymer electrolyte membranes offer an alternative by providing high ionic conductivity at small electrode gaps and enabling operation with gaseous and nonpolar media; however, membrane contamination and electrode durability remain major barriers to broader use in organic electrosynthesis.

Comparable challenges were once encountered during the development of classical chemical manufacturing, where the transition from fundamental chemical research to applied engineering ultimately enabled industrial implementation. A similar trend is now envisioned for organic electrosynthesis, with process engineering expected to play a central role in translating laboratory-scale findings into robust and efficient industrial technologies.

From a process engineering perspective, cell designs should permit easy handling and maintenance (cleaning, minimal consumables), ensure efficient mass transfer and gas removal, and provide uniform electric fields and materials compatibility at target temperatures; even near-ambient chemistries can experience temperature rises in larger cells due to ohmic heating [436–438].

In recent years, materials advances, and electrochemical process engineering have addressed these scale-up constraints and improved understanding under technical process conditions, leading to (micro) reactors tailored to specific electrosyntheses with defined flow fields, turbulence promoters, and tailored electrode geometries [429,439–442]. Process engineers have focussed onto all aspects, such as improving space-time yield, selectivity, conversion, energy efficiencies, designing reactors that enhance mass-transport rates and/or promote efficient gas removal, while maximizing the electrode-area-to-electrolyte-volume ratio [424,443].

To enable rational design and scale-up, process engineers developed model-based methods to quantify electrode and cell behaviour [424]. However, continuum modelling of electro-organic processes remains uncommon due to the large diversity in chemical processes, the absence of standard models, and the relatively narrow set of reactions studied at technical scale. Most studies adopt approaches from water electrolysis and fuel cells, typically employing lumped kinetic descriptions and only rarely resolving the multistep mechanisms characteristic of organic electrosyntheses. At the continuum scale, models are grouped into: (i) kinetic models [444,445], which capture reaction kinetics and near-electrode transport; (ii) fluid-dynamic models [446,447], which resolve convective flow and concentration fields in cells; and (iii) process models [448,449], which analyse the full process including balance-of-plant components. Notably, although most electro-organic syntheses are performed at laboratory scale, the modelling literature has focused predominantly on undivided flow cells rather than the lab-typical beaker or H-type cells.

Cells for organic electrosynthesis can be classified as:

(i) turbulence-enhanced systems (pump cell [450], bead-rod cell, vibrating electrodes [451], and continuous stirred tank reactor (CSTR) configurations, rod-in-tank and rotating-cylinder-operated in single-pass, cascade, or recirculation modes [452]);
(ii) small-volume cells with large electrode area and minimized interelectrode distance (capillary-gap reactors [453,454], rotating electrode cells [455], Swiss Roll cells [456], extended-surface electrolysis [457], and parallel-plate flow reactors in single-cell or stack configurations, run in single-pass for longer residence times – useful for unstable products [458] – or at higher flow rates in recirculation to suppress gas holdup and residence-time fluctuations [437,438,450,459,460]; and
(iii) reactors with 3D-structured electrodes providing large specific surface area and defined hydrodynamics (fluidized bed cells [461,462], porous flow cells [463], packed-bed cells [464], rolling tube cells [435]; for gas/liquid reactions, cells with porous gas-diffusion electrodes [465]. Beaker-type batch cells (plate-in-tank or rod-in-tank) remain widely used and are straightforward to scale by adding electrode area, but they suffer from non-ideal mixing, inhomogeneous fields with rod electrodes, and unfavourable electrode-area-to-volume ratios [452, 466–471].

Recently, 3D printing of (metal) electrodes with adjustable surface, porosity, and flow profile has yielded new electrode structures and compositions [472,473], including electrodes incorporating carbon or conductive polymers with metal powders [474,475]. Persistent needs include standardization of reactor setups, reproducibility and transferability across scales, and comprehensive cell and process models to identify operating windows and enable reliable scale-up.

With recent advances in materials and reactor design, and in light of increasingly stringent climate-change regulations in chemical manufacturing, there is a clear opportunity to convert conventional processes to electrochemical technologies [476]. Realizing this potential will depend critically on electrochemical reactor engineering: standardizing reactor setups and operating procedures; establishing reproducible benchmarks (space–time yield, selectivity, conversion, energy efficiency); and applying validated quantitative kinetic and digital methods to define operating windows and ensure reproducibility across scales. Methods already proven in chlor-alkali electrolysis, CO_2 reduction [477–479], biomass electrolysis, and water splitting provide transferable methodology [480]. In parallel, kinetic studies on defined cell designs should resolve the coupled charge, mass, heat, and momentum transport phenomena and link them to electrode behaviour, enabling the design of robust reactors and production processes. Organic electrochemical technologies remain a relatively untapped field for solutions from which industry can benefit [481]; targeted process engineering contributions are central to moving more reactions to technical maturity.

Lastly, to guide sustainable decision-making, life cycle assessment (LCA) can be used to quantify the environmental impacts (CO_2 emissions, water consumption, resource depletion) of manufacturing

reactors and processes, as well as their subsequent operation for their existence. For example, differences in national fuel mixes and associated CO_2 emission rates between countries may affect decisions about where manufacturing and process operations are located, in addition to techno-economic process assessments that may ignore environmental externalities.

3.4. Electrochemical materials processing and corrosion protection

Degradation of materials is an important phenomenon causing important losses to the global economy caused either by the need of regular replacements or by the accidents related to the loss of functional material properties. Beside these functional aspects, materials treatment for aesthetic purposes also represents an important industry.

3.4.1. Materials processing

The role of electrochemical engineering in materials processing and protection has often been underestimated. Part of the reason is that electrochemical materials processing can appear under headings such as electrodeposition, surface technology, additive manufacturing or electropolishing. Materials protection is often classified under corrosion. This divides the common theme across several subjects, including chemistry, physics, material sciences, electrochemistry as well as surface engineering. For example, a simple search on Scopus®, using keywords such as electrodeposition, electroplating, electroforming, as well as deep eutectic solvents (DESs) or metal-in-salt electrolytes show that papers submitted with a keyword 'electrodeposition' has increased substantially since the 1990s. However, the more common industrial nomenclature of electroplating used in the coatings literature, seems to capture less citations. Niche applications, such as electroforming, also remain less popular, although their role in additive manufacturing is becoming more important.

Double keyword searches, useful to examine sectors in which electrodeposition is making a mark, were also carried out. The majority of publications related to electrodeposition is related to fabrication of functional alloys for microelectronics [482], medical sensing [483], aerospace sectors [484] or energy applications to synthesize solid state catalytic or battery materials [485]. Recent advances, such as electrochemical deposition from ionic liquids (ILs) and DESs constitute a small fraction of those papers [486].

Electrodeposition research has made great strides in the microelectronics sectors, despite the shrinking dimensions of electronic components [482], devising new methods for deposition on chips and circuit boards [487] whilst facing up to challenges of more restrictive environmental regulations, limiting the use of toxic materials such as lead, cadmium and chromium *etc.* [488] by generating lead-free solders [489–493]. This latter problem continues in sectors requiring smooth, dense and uniform films, which for their formation need chemical additives as components of most industrial electrodeposition baths. However, presently such addition agents are under scrutiny because of their potential dispersal into the environment. Hence, bio-genic chemicals, such as glycine, alanine and valine [494], thiourea and allyl thiourea [495] have been investigated as substitutes with lower environmental impacts to replace more toxic ones in well-established processes.

A similar, but different challenge over the past quarter century has been to achieve super-conformal electrodeposition to fill through-silicon vias (TSVs) in integrated circuits or various types of vias in printed circuit boards (PCBs) [496]. When electroplated, usually with copper, vias connect different levels of multi-layered devices or boards and usually have high depth-to-width ratios. For vias to fill correctly, special chemical systems are needed to fill holes from the bottom, whilst restricting growth from the sides and at the top. This is achieved by using a combination of suppressors and catalysts, which can access different parts of the surface, whereby selective suppression and activation of deposit growth is achieved [497]. Researchers have extended concepts from existing understanding of levellers and inhibitors reported in the electroplating literature [496–500], by including the role of surface curvature and associated activity, and established mathematical models to validate and predict the formulation of electrolyte and electrochemical conditions [501,502] to achieve conformal or super-conformal growth.

A major user of electrodeposition has been the energy sector, in which there is/has been a high demand for new catalytic materials for electrolysers and batteries. Researchers have searched for methodologies to produce materials of high specific surface area (vs. volume) [486, 503], higher catalytic activity [504], increased stability [505] or robustness. These properties were achieved by nano-scale structuring of the same material or manipulating the surface of an alloy to enhance its properties [505,506]. Suggestions of new battery systems based on Al-Imidazolium systems [503,507] or Na-ion [486] for Li batteries has also been made, which require specially tailored electrode materials as well as architectures.

The venture into electrodes in non-aqueous electrolyte solutions has sparked the exploration of a wide range of ILs including DESs for electroplating Fe, Cu, Ni, and their alloys [508–510] have been synthesized using DESs. DESs have been popularised because they hold the promise of extending the window for metal deposition by eliminating water breakdown which is usually encountered when aqueous systems are used for metal deposition [508]. This would allow light metals such as aluminium and titanium to be deposited; in addition, metals such as chromium and platinum can be plated from DESs that are accompanied by excessive hydrogen evolution in aqueous solutions. Although DESs have been reported to obtain a range of metals and alloys, recent studies have revealed that further research is needed to exploit DESs full potential, partly because it has been shown that DESs break-down during metal deposition [511–513] or that the solutions are unstable, being hygroscopic [514], or corrosive [515].

In addition to developing new materials, recent research on metal deposition techniques are focusing on the ability to extract metals using unusual aprotic solvents – such as DES and metal-in-salt electrolytes [516], and then electrodepositing metals from these systems. Metal-in-salt electrolytes are similar to brines, and work in a similar way to DESs. In these systems, the high ionic content forms an intricate network such that water remains bound. In the absence of free water proton reduction or water breakdown cannot occur during metal deposition [517]. While some of these approaches have been exploited for the recovery of iron [516], challenges remain in their full exploitation [518].

Mathematical modelling has enabled predictions [497,498, 519–521] of current distributions in complex substrates. These have been exploited in industry to design new equipment or develop protocols for product fabrication [522]. New processing equipment and technology encompass the use of novel modes of agitation, especially ultrasonics [523,524], and the continued use of current pulsing [525] has been used for electrodeposition, and novel reactor arrangements have been proposed [526]. Some manufacturing industries have adopted these methodologies successfully to devise new production methods [527,528]. Nanotexturing of iron and steel has also been achieved through intelligent manipulation of anodising equipment and protocols [529,530], which are useful for energy and medical applications.

In the future, further transformations may be required with the advent of Industry 4.0 [484,516,517,522]. Recent research has shown that a greater understanding of electrolyte [514] and anode reactions [531] needs to be carried out to improve the processes further. The growing use of critical elements, such as neodymium, Nd [532], or other rare earths may be useful in electric vehicle motors, will require tailored approaches to fulfil bespoke requirements. These may be more achievable with new aprotic electrolytes, require new reactors, careful designing or protocols electrodeposition.

3.4.2. Corrosion protection

Corrosion is a significant challenge to most industrialised economies

globally because it causes disasters and massive financial losses. Corrosion is so prevalent and takes so many forms depending on the nature of materials used, applications, and the surrounding environment. The latest surveys show that the total worldwide, direct annual estimated cost of corrosion (essentially materials, equipment, and services involved with repair, maintenance, and replacement) is ca. 3×10^{12} US$, or ca. 3–4 % of the global gross domestic product (GDP). This figure does not include the environmental damage, waste of resources, loss of production, or personal injury resulting from corrosion. Different sectors (and related industries) are mentioned in Fig. 13 [533], particularizing pipelines, bridges, and public buildings to vehicles, water and wastewater systems, hydrogen infrastructure, electricity production and storage, chemical, petrochemical, and pharmaceutical industry, smart home and city appliances, electronics, batteries, sensors, and even nanotechnologies.

There are different techniques to control corrosion, the most common being the use of coatings and cathodic protection. However, apart from improving the present technologies through selection of materials and more efficient coatings (like self-healing coatings) for a particular application, investment in new technologies for biodegradability and programmable corrosion is also needed.

This review concentrates on the challenges associated with the energy/digital transition, namely the challenges for the corrosion and protection industry associated with building climate-resilient energy systems and infrastructures from the engineering point of view. Some of the problems that are found presently, from the assembly of structures for photovoltaics (PV) [533,535] to the building of light automobiles and aircrafts [536], arise from the use of multi-material combinations envisaged, involving different metal alloys, fibre-reinforced plastics and other component materials (*e.g.* glass). This can lead to problems well reported in the literature such as galvanic corrosion. Other issues can be found on the durability of metallic materials used in solar thermal energy systems, which are exposed to different heat transfer media (molten salts, organic fluids, or liquid metals among others) [537]. Furthermore, the improvement of the durability of semiconductors used in PVs [538], as well as of electrocatalysts used in electrochemical water-splitting [539] are amongst the problems, for which corrosion scientists are expected to provide solutions.

Additive manufacturing (AM) is another important topic in the context of energy/digital transition that is having a massive impact in industry. AM offers the opportunity to fabricate components with complex designs in short times, and with minimal material waste generation [540]. However, when using AM with metals or alloys, not only are the alloys obtained revealing unique properties in terms of microstructural characteristics (surface roughness, porosity, residual stress, cellular structures, non-equilibrium microstructures), requiring understanding of their corrosion performances, but also there is need for development of surface treatments and coatings capable of controlling thickness, porosity and other properties throughout the whole component geometry [541].

3.4.2.1. Corrosion protection in batteries. Specific corrosion requirements must be met in the case of batteries, due to the redox reactions taking place during charging and discharging. An advanced protection of the materials can be achieved by application of a specific functional coating (self-healing, nanotechnologies *etc.*). Materials are required to ensure more stable cathode | electrolyte interphases and anode surface coatings for more stable SEIs, together with decreased probability for releasing gaseous products [542]. Coating degradation, growth of Li dendrites (Li-batteries), corrosion of aluminium collectors, cementation of copper leading to bimetallic corrosion, among others have all been identified as corrosion mechanisms, which shorten the battery life in service [542] (Fig. 14). Monitoring the condition of the electrode materials by means of intelligent sensors, identifying critical corrosion parameters in the battery are also key factors to predict battery lifetime. All these approaches can help to avoid dangerous events resulting from degradation of the materials and can further improve the safety of the whole battery pack [542].

3.4.2.2. Corrosion protection in hydrogen technologies. Advanced materials developed for a new generation of electrolysers need to be tested for safety and increased lifetime. In this regard, the development and implementation of advanced methods for prediction of the hydrogen embrittlement, in both laboratory by analytical methods, and in-service prototype, are equally important; processes related to degradation of materials when in contact with hydrogen are very complex. Hydrogen embrittlement is one of the key and critical issues with challenges in mathematical and thermodynamic modelling; quantum chemical calculations of interactions of hydrogen with physicochemistry of materials and/or environmental contaminants, aiming to predict material lifetimes [542].

3.4.2.3. Modelling and data-driven tools in corrosion. Models of corrosion processes based on understanding of physical processes occurring have been developed and reported [544] over several decades to guide materials selection and aid development of more corrosion resistant alloys and protective systems. Examples in the literature involve Density Functional Theory (DFT) used to identify more efficient corrosion inhibitors [545] or molecular dynamics (MD) to understand nanocontainer's function [546].

On the other hand, the implementation of high-throughput techniques to aid characterisation and corrosion monitoring is becoming more common, opening opportunities for the development of what is today recognized as data-driven materials science [547], with the data available enabling machine learning [548]. Thus, there is a necessity to acquire data-science capabilities and contribute to the education of new generations of electrochemical engineers capable of dealing with hybrid theoretical-experimental approaches in the field of corrosion and corrosion protection.

3.4.2.4. Self-healing coatings. One of the most widely adopted strategies

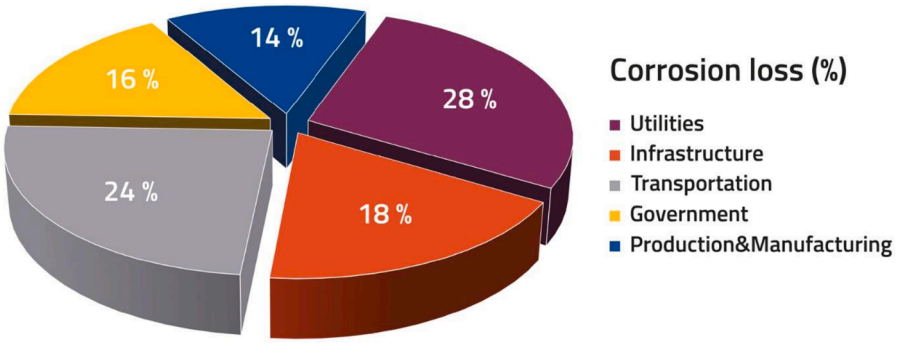


Fig. 13. Cost of corrosion in different sectors [534].

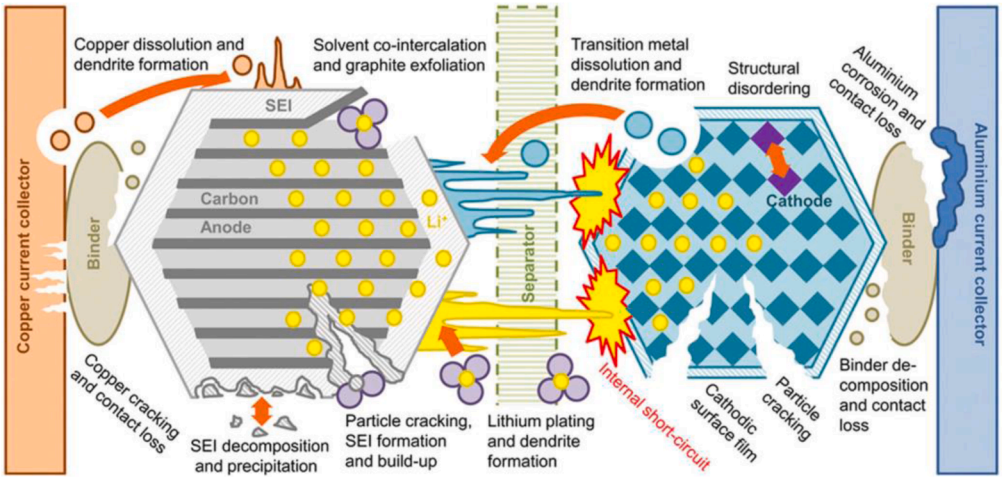


Fig. 14. Different mechanisms of degradation inside Li-ion batteries [543].

for protecting metal alloys from corrosion degradation involves the application of protective coatings. In the past, Cr^{VI}-based pigments were incorporated into coatings to provide active corrosion protection in the event of coating failure. However, the significant toxicity and carcinogenic effects associated with Cr^{VI} [549] led to its prohibition, prompting a shift toward more environmentally sustainable approaches. This transition has spurred extensive research within the corrosion science and engineering community. Over the past two decades, this research has driven the development of self-healing coatings – systems capable of responding to environmental triggers linked to coating damage, corrosion initiation, or both [550]. Despite the promising results reported in the literature, widespread adoption of self-healing technologies in the coating industry remains challenging. Barriers include the complexity and high cost of industrial implementation, as well as limited compatibility between self-healing additives and existing coating formulations [551]. Hence, electrochemical engineers play a pivotal role in advancing coating technologies that are not only robust under harsh conditions but also environmentally benign and industrially viable.

3.5. *Interfaces with biology and health*

Electrochemical engineering made a remarkable entry into the domain of biotechnology at the beginning of this century with the emergence of microbial electrochemical technologies (METs). Beyond the field of METs, electrochemical engineering could provide valuable fundamental and technological support to many other areas of biotechnology, biology and medicine, but these fields remain little explored so far. Some topics for which electrochemical engineering may be of great help are discussed here, but the opportunities are so numerous and diverse that the list cannot claim to be exhaustive.

3.5.1. *Biosensors*

Electrochemical biosensors are the most obvious historical successes of the association of electrochemistry and biology [552]. The electrochemical detection, quantification and characterization of proteins, deoxyribonucleic acid (DNA) and other biomolecules is a burgeoning domain. Such biosensors have started to penetrate core fields of biology and medicine, such as enabling the distinction between different cell lineages for advanced diagnostic purposes and even contributing to therapeutic strategies [553], detection of viruses [554] (the consequences of covid-19 in 2020 highlighted the importance of this item) and next-generation cancer diagnosis [555]. Electrochemical biosensors are now foreseen as the basis of field-deployable analytical instruments, in particular point-of-care biosensors [556], which are expected to revolutionize personal health care, *e.g.* with mobile phone-based biosensing [557]. Applications in environmental monitoring and food quality control are also noteworthy [558].

Widespread progress is being made towards miniaturized electrochemical devices [559], with the intimate association of nanomaterials and biomolecules. Carbon-based nano-materials (carbon nanotubes, graphene, graphene oxide, fullerenes) hold a prominent place among nano-scale materials [560,561]. Nanoparticles of noble metals and polymer nanomaterials are also commonly used and novel bio-nanomaterials have been specifically developed for application in biosensors [562]. Aptamer-based biosensors deserve special attention [563] because of their high affinity, selectivity, and specificity, which are equal or even superior to those of antibodies [562].

In parallel, dedicated electronics are being developed, mainly based on field effect transistors [564], with wearable and flexible electronic systems [565], tending towards the concept of nano-architectonics [566]. Biosensors have long been foreseen as pioneers to open the way to nano-bioelectronics [567], including such futuristic ideas as intra-cellular sensing [568].

Biosensors using microbial biofilms can be considered as a part of MET, but it makes sense to pay specific attention to them here. In these devices, the microbial biofilm that constitutes the recognition element self-organizes on the electrode surface. Such biosensors were initially proposed as biofouling monitoring systems [569,570] and later led to microbial fuel cell sensors [571], which can be considered as self-powered biosensors [572,573].

The association of biologists, electrochemists, experts in nanomaterials and electronic engineers has been remarkably successful, but electrochemical engineering could help in numerical modelling [574] to optimize the design and to model the transient behaviour of biosensors in order to decrease their response time [575].

3.5.2. *Enzyme-catalysis in fuel cells and electrosynthesis cells*

Enzyme-catalysis represents an intensively studied process due to its very high selectivity and potential to convert waste materials to the energy and/or in valuable products. Hence, the following sections focus on fuel cells and selected examples of electrosynthesis.

3.5.2.1. Enzymatic fuel cells (EFC). EFCs are often called biofuel cells, although this term is quite confusing because it should include microbial fuel cells on the one hand, and 'biofuel cells' generally do not use biofuels on the other hand [576]. EFCs [577] work under mild conditions of temperature and pH, and use fuels from possible non-fossil sources such as alcohols and sugars, which cannot be exploited easily with metallic catalysts. Oxidoreductases (enzymes that catalyse redox reactions) are highly selective. The anode and the cathode, each equipped with the

appropriate oxidoreductase, consequently can be incorporated in a single membrane-less cell fed with a mix of fuel and oxidant. Finally, the biodegradability of the enzymes may allow disposable biodegradable fuel cells to be designed. In contrast, when the production, extraction and purification steps of oxidoreductases are analysed, it is not fully obvious that the 'green technology' label, sometimes claimed because enzymes are biological compounds, is justified.

EFCs produce modest power densities, with few surpassing 1 mW cm^{-2} [577]. For example, 2.9, 3 and 6.1 mW cm^{-2} are among the highest power densities obtained with sucrose [578], glucose [579] and hydrogen [580], respectively. Actually, their main drawback is not the modest power densities they provide, but the poor stability of oxidoreductases. Power outputs generally are not sustained for more than a few hours, or a few days at best [581].

Electrical energy is too inexpensive for the expensive redox enzymes to be justified for mass production. EFCs have been proposed for powering low-power electronic devices (LEDs, mobile phones, laptops, etc.) but strong specific advantages still need to be proposed to balance the stability, low cost and ease of use of conventional batteries. Specific niche applications should be found, *e.g.* where disposable fuel cells are needed, when the use of alcohols or sugars is required, for self-powered biosensing, bioelectronics [582,583], *etc*. EFCs using glucose as the fuel have been regarded as possible implantable sources of energy [584]. However, this application would pose several medical problems related to the implantation of an electrochemical system directly in the bloodstream: consumption of glucose and oxygen in unstable patients, possible generation of reactive oxygen species that are deleterious to cells, possible release of compounds (*e.g.* nanoparticles) into the bloodstream, *etc*. These major medical issues may preclude their real implantability.

Currently the issues of oxidoreductase cost and stability need to be solved in order to open space for electrochemical engineering to scale-up and intensify the process. This will help to identify real-world applications justifying such sophisticated and fragile fuel cells. In the particular case of implantable devices, by working in close association with physicians, electrochemical engineers could build a systemic approach in order to assess the real applicability of the concept.

3.5.2.2. Enzyme-catalysed electrosynthesis. Oxidoreductases are attractive catalysts for the biosynthesis of chiral compounds and polymers [585,586]. Nevertheless, their use at industrial scale remains challenging because they require cofactors, often nicotinamide adenine dinucleotide (NAD) and the related NADP, which are too expensive to be used in stoichiometric ratios. Cofactors need to be regenerated by reduction or oxidation, a major impediment to the use of oxidoreductases as isolated enzymes in industrial processes, so biosyntheses involving NAD(P) are generally implemented with living cells [585, 586].

The electrochemical regeneration of cofactors would afford great advantages in comparison to cell-based processes by considerably simplifying the composition of the media and thus minimizing the complexity and the cost of the downstream separation and purification steps. Only electrons are supplied to, or removed from, the system and this results in limited production of by-products. Generally, only oxygen or hydrogen is the by-product at the auxiliary electrode. A large range of oxidoreductase-catalysed reactions could benefit from the electrochemical regeneration of the cofactors [587–589] and specific reactors are starting to be designed [590,591].

The electrochemical control of the 'oxygen/hydrogen peroxide' couple is also worth considering. Electrons must be supplied to some enzymes, such as peroxidases [589] and cytochrome P450 [587], in the form of hydrogen peroxide, but its concentration must be controlled accurately because these enzymes are sensitive to oxidative degradation. Consequently, in situ generation of hydrogen peroxide by oxygen reduction could be the ideal way to deploy these enzymes [587,589, 592]. Conversely, the electrochemical oxidation of the hydrogen peroxide produced by glucose oxidase has been shown to stabilise the enzyme and enhance its production rate [593]. Flavin can also be a valuable electron shuttle in the context of electrosynthesis. For instance, the regeneration of flavin has led successfully to the reduction of methaemoglobin to haemoglobin in a lab-scale reactor [594].

Catalysis of the electrochemical reduction of carbon dioxide by oxidoreductases has yielded formate ions, ethane or propene, either by using a redox mediator or by direct electron transfer from the electrode to the enzyme [595,596]. Similarly, dinitrogen can be converted to ammonia [597].

Although the concept is a long-standing one and successes have been achieved at the scale of laboratory reactors [590,592,593,598], this research domain deserves to be more vibrant. The mass production of low-cost basic chemicals from CO_2 or N_2 cannot justify such expensive processes. Electrochemical engineering may help to reorient the topic towards the production of high-value added compounds rather than basic chemicals. In this context, electrochemical engineering should have a key role to play in reviving the research area by designing efficient pilot scale trials. Theoretical and experimental bases are available to start scaling up some model reactions.

3.5.3. Microbiologically influenced corrosion

The spontaneous development of microbial biofilms on metallic materials can drastically enhance their corrosion. So-called microbiologically influenced corrosion (MIC), or biocorrosion, is known to be the direct cause of catastrophic corrosion failures, resulting in damage evaluated at several billions of euros per year [599,600]. Anaerobic MIC has been attributed mainly to the action of sulfate- and thiosulfate-reducing bacteria but, in recent years, the range of possible mechanisms has been widening, in particular with the possibility of direct electron transfer from the material to the biofilm [601,602]. Mechanisms of aerobic MIC are even less clear and are still under debate with many possible ways of occurring [603].

A recent review article has pointed out the lack of significant advances made these last 20 years in understanding MIC and being able to predict it [600]. The article emphasizes that most studies are carried out in laboratory conditions, far from the natural or industrial conditions in which MIC occurs. The main advice of the article is to prefer 'a holistic, proactive approach to MIC in which an entire system is considered, monitored and improved'. This sentence seems sufficient to show the key role that electrochemical engineering should play if the objective is to understand and mitigate real MIC.

In essence, MIC is a complex process that results from many local multiphysics interactions (electrochemical kinetics, chemical kinetics, microbial metabolism, surface material evolution, mass transfers, shear stress, etc.), which occur in heterogeneous environments with sharp gradients of chemical composition, including oxygen and pH. The capacity of electrochemical engineering to unravel and model such complex coupled steps should be a core motor in deciphering MIC and finally finding innovative ways to monitor and mitigate it.

3.5.4. Microbial electrochemical technologies

Microbial biofilms may be responsible not only for undesired processes, but may also be used as biological electrocatalysts for various processes. These, together with other, non-conventional microbiological electrochemical technologies is the subject of this section.

3.5.4.1. Conventional electrochemical processes with electroactive biofilms inside. The catalytic layer in microbial electrochemical technologies (MET) devices is a microbial biofilm that self-organizes on the electrode surface and self-acquires electrocatalytic properties [604,605]. In contrast to enzymatic electro-catalysis, biofilm-based catalytic layers are low-cost, easy to prepare and self-sustaining. The ease with which electroactive biofilms can develop on electrode surfaces has led

researchers to revisit all possible electrochemical processes by integrating microbial electrocatalysis inside [606,607].

MFCs are the flagship MET [608,609]. The electroactive biofilm on the anode catalyses the oxidation of organic matters, such as alcohols, sugars and, more interestingly, volatile fatty acids that can come from waste and sediment. Thus, it is possible to produce power from waste [610]. Microbial anodes can also be used in microbial electrolysis cells (MECs) that produce hydrogen at the cathode [611]. Replacing the oxidation of water used in water electrolysis by the oxidation of acetate decreases the equilibrium cell potential difference by one order of magnitude (0.12 V instead of 1.23 V) [612], which should bring great benefit in terms of cost of hydrogen produced. The decreased cell potential difference afforded by MECs has also been contemplated for other applications, including methane production [613,614] and metal recovery [615]. At the cathode, electroactive biofilms have been shown capable of catalysing the production of chemicals, particularly by reducing carbon dioxide [616,617].

MET has opened up very appealing perspectives for a huge number of applications, including such ambitious objectives as massive production of electrical energy and mitigation of global warming by converting carbon dioxide to renewable fuels. Actually, basic knowledge on extracellular electron transfers between microbial cells and electrodes is growing rapidly [604,605], revealing fascinating new aspects of microbial life. However, in spite of the great fundamental advances, the technological promises seem to be a very long way from being fulfilled. Scaling up MET to industrial-sized pilot plants has never been successful so far, in spite of many attempts [612,618]. For instance, after around 20 years of research, power densities produced by MFCs have yet to exceed a few W m^{-2} [618,619].

Several severe bottlenecks have been identified [162,612]. First of all, urban wastewaters, which are the most usually targeted electrolyte solutions, have very low ionic conductivities (generally < 0.5 S m^{-1}), which prevents high current densities from being achieved in conventional electrochemical reactors. Oxidation of organic matter at the anode causes local acidification, which inhibits the microbial catalysis. Conversely, alkalinisation of the cathode in culture media that contain calcium and magnesium cations leads to rapid biofouling of its surface. In the case of a MFC, oxygen reduction at the cathode is a severe rate-limiting step, because there is no efficient catalyst of oxygen reduction at the close-to-neutral values of pH required for the microbial anode to work. Some of these bottlenecks can be partly overcome, for example, by using saline electrolytes in order to increase ionic conductivities of electrolyte solutions [620]. Thus, a current density of 90 A m^{-2} has been achieved in a MEC, but biofouling of the cathode remained a severe hindrance after a couple of weeks of operation [621].

A glance at the mechanisms of the microbial cathodes for CO_2 reduction shows that the main role of the electrode is to produce hydrogen, which is then used by the microbial cells to hydrogenate CO_2. Hence, it would be more suitable to scale up the process in two separate steps: abiotic water electrolysis in a conventional electrolyser, coupled with the downstream, microbially-catalysed hydrogenation of CO_2 [622].

In this context, electrochemical engineering can unravel the mechanisms of extracellular electron transfer in microbial biofilms and judge which discoveries have the potential to transition towards practical applications For instance, promising MFC applications may be considered for low power production, *e.g.* in self-powered biosensors [572,573] such as stunning new applications like sensors fed with urine [623] or sweat [624].

3.5.4.2. Non-conventional microbial electrochemical technologies. MET has given rise to several new electrochemical processes specifically dedicated to microbial electrocatalysis, which were not anticipated in the scope of conventional electrochemical processes:

(i) Electro-fermentation: the capacity to drive fermentations by a non-Faradaic electrochemical process [625],
(ii) Microbial snorkel: a system that can be considered as a microbial anode short-circuited with a cathode [626]. It can be implemented as a simple conductive bed in a wetland for wastewater treatment [627,628]. The bottom of the bed, in the anaerobic zone of the bioreactor, is the anode, while the upper part, in the aerobic zone, is the cathode. Electron transfer rates in such short-circuited systems are maximised, thus maximising the abatement of the organic matter content of the waste.
(iii) Cable bacteria: filamentous bacteria able to transport electrons over centimetre distances through the anoxic-oxic interface of mud or marshland [629]. They can be considered as the natural version of a microbial snorkel [630,631].
(iv) Electron transfer between different bacterial species, also called direct interspecies electron transfer (DIET): these electron transfers from cell to cell have been shown to be mediated by conductive particles [632,633]. This process may be very important in anaerobic digestion for methane production and also could operate in the undesirable methane release from wetlands.
(v) hybrid microbial catalysis: catalysis achieved by coupled microbial cells and metallic compounds [634].

Most of these processes are characterized by their low-cost and low maintenance requirements, so they can be scaled up to large sizes even if the local current density remains modest. They are examples of groundbreaking concepts that should boost the development of MET in unforeseen ways. electrochemical engineering should have key roles in understanding, optimizing and developing these innovative fields of investigation.

3.5.5. Medicine

The role of electricity in the development of living tissues has been hypothesised for a very long time [635]. As reviewed more recently [636,637], endogenous electric fields are now known to play many essential roles in living organisms, not only for the transmission of nerve impulses or muscle contraction, but also in controlling cell morphology, gene expression and cell proliferation. Effects on tumour growth have also been speculated [638,639]. Electric potential gradients have been found to be a major motor of wound healing [640,641] by driving cell migration towards the injury [641,642]. Experiments performed on aquatic worms [643] and frogs [644] showed that 'bioelectric signalling' was a key parameter in the formation and location of organs [643,645]. The concept of 'bioelectric code' has been launched [646] as a possible explanation for pattern regulation in living organisms. Direct electron transfer between mammalian cells and electrodes has recently been achieved, demonstrating that even the core process of cellular respiration can be accessed through electrochemistry [647].

The use of external electrical stimulation is now well-established in medicine [636]. Electrical stimulation is largely used to fix bone defects and repair fractures by promoting osteogenesis [648]. It has also been tested successfully on small animals to heal complex wounds [649]. In addition, electric stimulation is envisaged as a way to control the proliferation, differentiation and spatial location of stem cells [650–653].

Electrochemical engineering has approached the medical domain with biosensors and electrochemical devices for the application of electric stimuli [654]. It is now becoming increasingly obvious that essential functions of living organisms, including the human body, are controlled by endogenous electrical potential gradients and endogenous electric fields. This is still terra incognita for electrochemical engineers, who could play key roles in investigating such complex 'electrochemical processes' as living organisms, with the prerequisite of an intimate partnership with medicine.

3.6. Technology transfer – from fundamental research to industrial process

Technology transfer represents the 'master discipline' of electrochemical engineering. It is a synthesis of the all the aspects mentioned in the previous sections. It may be divided into the several consecutive steps important to achieve successful final result. The transfer steps will partly differ for individual types of applications, like large scale electrolysis or mass production of sensors, but the framework structure may be summarised as follows.

(i) Analysis of the fundamental research results to judge the application potential of the phenomena studied.
(ii) Definition of the application field and scale expected.
(iii) Experimental verification of the materials used and process conditions required, including input parameters for follow up steps.
(iv) Fundamental economic analysis of the solution proposed.
(v) Definition of the type of the cell and process conditions on the base of the experimental data available.
(vi) Scale-up of the process to the pilot scale.
(vii) Experimental validation of the laboratory scale data on a pilot scale.
(viii) More detailed economic analysis, including legislative and regulatory framework.
(ix) Design of full scale process.
(x) Construction, validation and final tuning of the process.

Modern tools of mathematical modelling and techno-economic analysis facilitate the entire process more rapid and efficient. This makes the technology transfer time and cost intensive. Careful analysis in every of its step is necessary prerequisite to spare any unnecessary costs. Important is also continuous communication with all stakeholders. It includes not only end-users of the technology, but also authors of original idea, producers of the individual components, including balance of plant, material engineers, environmental impact specialists and last, but not least, customers interested in the final product. The role of electrochemical engineering is inevitable. Beside their crucial role in analysis of experimental data and performing scale-up process, they provide important input for and coordinate remaining activities with target to achieve technology characterised by high efficiency and required economic and environmental characteristics.

4. Summary and outlook

Probably the most visible application of the whole scope of electrochemical engineering presently is connected with the transition to all-electric societies, which are becoming more dependent on electrochemical technologies to enable them to achieve national sustainability targets and to mitigate historical effects of fossil fuel-based industries on the global climate. This review aimed to demonstrate the critical role of electrochemical engineering in the development and up-scaling of electrochemical systems, hopefully leading ultimately to their deployment to address such global societal problems. In addition, other electrochemical technologies such as safe water and environmental protection in general, are impacted by this transition putting more stress on flexibility and efficiencies of the individual required technologies. Whereas the original discovery or conception of potential solutions of such problems may originate from electrochemical science, early integration of electrochemical engineering with that science aids successful development of electrochemical processes, by judicious reactor and process design aided by modelling; *i.e.* the science and engineering R&D partially in parallel rather than in the more conventional series connection.

What is the outlook of electrochemical engineering for the near and more distant future? Rapidly expanding computational power coupled to artificial intelligence will enable mathematical simulations of far greater complexity than hitherto, achieving multi-scale behaviour predictions from atomic, to laboratory prototype, to pilot plant and even to industrial scale with adequate precision, enabling *in silico* optimisation of electrochemical systems to be achieved. However, experimental validation of such predictions is often cost- and time-constrained, precluding extensive experimental exploration of the complex, multi-dimensional behaviour typical of electrochemical systems. Hence, computational predictions will be used for experimental design to focus experiments on more critical areas of parameter space at appropriate scales, to interpret and analyse experimental results and to provide greater confidence in up-scaling. Computational models could also be used to drive 3D printing of electrodes, reactors and other components, thereby decreasing development times and costs. Hence, there are many reasons to be optimistic about the future of conception and development of engineered electrochemical systems aimed at addressing global energy, environmental and related issues

CRediT authorship contribution statement

A. Bergel: Writing – review & editing, Writing – original draft. **H. Bergmann:** Writing – review & editing, Writing – original draft. **K. Bouzek:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization. **M.G.S. Ferreira:** Writing – review & editing, Writing – original draft. **G.H. Kelsall:** Writing – review & editing, Writing – original draft, Conceptualization. **U. Krewer:** Writing – review & editing, Writing – original draft. **G. Kreysa:** Writing – review & editing, Writing – original draft. **F. Lapicque:** Writing – review & editing, Writing – original draft. **M. Paidar:** Writing – review & editing, Writing – original draft. **M. Prokop:** Writing – review & editing. **M.A. Rodrigo:** Writing – review & editing, Writing – original draft. **S. Roy:** Writing – review & editing, Writing – original draft. **P. Röse:** Writing – review & editing, Writing – original draft. **G. Schmid:** Writing – review & editing, Writing – original draft. **J. Tedim:** Writing – review & editing, Writing – original draft. **T. Turek:** Writing – review & editing, Writing – original draft. **K.M. Vetter:** Writing – review & editing, Writing – original draft. **C. Weidlich:** Writing – review & editing, Writing – original draft.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

K.-M. Vetter and G. Schmid are previous employees of the 11Siemens Energy Global GmbH&Co.KG. This fact has no impact on their contribution to the manuscript. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2026.150160.

Data availability

No data was used for the research described in the article.

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