Review article

Electrified water treatment: fundamentals and roles of electrode materials

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Abstract

Electrified processes are a versatile way of removing a wide range of contaminants from water, especially those that are difficult to treat using conventional methods. Electrified processes do not need treatment chemicals and use renewable energy more efficiently. In this Review, we present the fundamental principles of several electrified water treatment processes, discuss the crucial role of electrode materials in the interfacial processes that drive contaminant transport and transformation, and comprehensively review the state of knowledge in electrode material development. Further, we analyse the advantages and limitations of current and emerging electrode materials and discuss strategies for developing advanced electrode materials. Finally, we outline a path towards next-generation water and wastewater treatment systems based on electrified processes.

Sections

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Review article

Introduction

Water is a precious resource for life. Supplying and distributing water safely was one of the greatest engineering achievements of the twentieth century[1]. Utilizing a combination of physical, chemical and biological processes, conventional water and wastewater treatment systems can remove or destroy a wide range of contaminants, including microorganisms, synthetic organic compounds and heavy metals[2] (Table 1). However, these systems face increasing challenges as our water sources become perilously scarce and befouled, requiring the removal of emerging and persistent chemicals that cannot be removed by conventional treatment processes. In addition, combating global climate change requires us to minimize energy and chemical consumption, and to use renewable energy in water and wastewater treatment. These new challenges have sparked strong interest in electrified treatment processes.

Electrified water treatment processes, defined as any electrode-based processes driven by an electric potential or current (potentially from renewable energy sources), use electricity directly to remove and degrade a wide range of organic, inorganic and microbial contaminants[3,4]. For example, electrochemical disinfection can inactivate bacteria and viruses through direct electric shock or in situ generation of chemical disinfectants (such as Cl_2)[5]. Electro-coagulation processes generate active coagulants in situ, which reduces the coagulant dosage needed and hence the chemical sludge produced compared with conventional coagulation[6]. Electrochemical advanced oxidation processes (EAOPs)[4,7] and electrochemical reduction processes (ERPs)[3,8–10] can transform toxic contaminants into benign species, such as CO_2, N_2 and H_2O, with faster kinetics and lower chemical consumption than is possible with conventional chemical or biological processes. Furthermore, electro-processes not involving redox reactions, such as electrosorption[11,12] and electrodialysis[13], can remove ionic species to realize water softening and desalination, and have the potential to replace reverse osmosis and thermal desalination technologies in some applications.

Compared with conventional water treatment processes, electrified processes have a number of advantages[14]. They remove contaminants by directly using the electrical potential or current applied or by generating chemical reagents in situ, avoiding the costs and risks to human health and the environment of chemical transportation and storage as well as disposal of the chemical sludge produced. Diverse process designs are available to treat a broad spectrum of contaminants, including mineralization of many refractory organic pollutants to form benign CO_2 and water. Furthermore, because of the fast reaction kinetics, a compact, modular reactor design can be used, and operation can be highly automated, with excellent tunability of the reaction rate or degree of treatment. Finally, the electrode or membrane materials can be designed to be selective towards target contaminants, decreasing energy consumption and allowing resource recovery.

In electrified treatment processes (with the exception of electrodialysis), contaminants are removed through interaction with the electrode. Therefore, low-cost electrode materials that have high activity, selectivity and stability (Box 1) are imperative to the successful application of electrified processes in water and wastewater treatment. In this Review, we discuss electrode materials used in major electrified water treatment processes, including EAOPs, ERPs and electrosorption, focusing on the interfacial processes that drive contaminant transport and transformation. We identify the limitations of current electrode materials and the associated challenges in electrified water treatment,
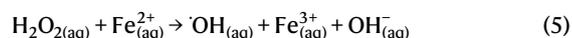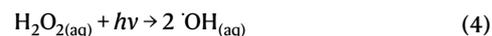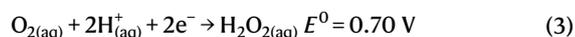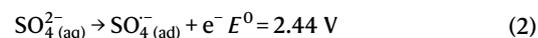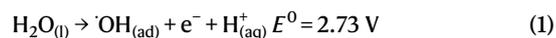
discuss how they can be addressed using novel materials and reactor designs, and recommend approaches that could advance electrified processes for water purification and resource recovery.

Principles of electrified processes

An electrified system uses a pair of oppositely charged electrodes – a negatively charged cathode and a positively charged anode – to conduct electrons to or from the target contaminant (such as in EAOPs (Fig. 1a) and ERPs (Fig. 1b)) or to drive the electrokinetic migration of charged species (such as in electrosorption and electrodialysis). When the electrodes are charged, an electric double layer (EDL) develops on their surfaces (Fig. 1c), through which the electrodes interact with the contaminant. The main electrified processes used in water treatment are described below.

Electrochemical advanced oxidation processes

EAOPs utilize the anode to conduct electrons away from an electron donor, which is oxidized in the process. The oxidation of organic contaminants in EAOPs may occur through direct oxidation and indirect oxidation (Fig. 1a). In direct anodic oxidation, electrons transfer directly from the contaminant to the anode[15]. For direct electron transfer to occur, the contaminant must lose some of its hydration water molecules and directly adsorb on the anode surface, that is, on the inner Helmholtz plane[16] (Fig. 1c). When the oxidation products desorb, the active anode surface sites are regenerated, allowing the adsorption and oxidation of more contaminant molecules. The reaction can be easily detected by cyclic voltammetry as a peak of rapid current increase during the anodic scans. Direct anodic oxidation usually yields products that are more biodegradable, but may not enact complete mineralization because the intermediates formed may not be electrochemically active in the working potential range[17]. Complete mineralization of organic pollutants in EAOPs often occurs through indirect oxidation, in which contaminants adsorb on the outer Helmholtz plane or in the diffusion layer (Fig. 1c) and not necessarily on the electrode surface. Consequently, electrons transfer from adsorbed water molecules or other radical precursors (such as persulfate) to the anode, generating strong oxidants[18], such as hydroxyl (equation (1)) and sulfate[19,20] (equation (2)) radicals (Fig. 1a) in situ. The oxidative radicals produced then diffuse back to the bulk solution and oxidize or even mineralize target contaminants to nontoxic species. Alternatively, hydrogen peroxide generated by the reduction of O_2 on the cathode (equation (3)) can be activated by ultraviolet irradiation (equation (4)) or the Fenton reaction (equation (5)) to form hydroxyl radicals.

$$H_2O_{(l)} \rightarrow {}^{\cdot}OH_{(ad)} + e^- + H^+_{(aq)} \quad E^0 = 2.73 \text{ V} \tag{1}$$

$$SO_4^{2-}{}_{(aq)} \rightarrow SO_4^{\cdot-}{}_{(ad)} + e^- \quad E^0 = 2.44 \text{ V} \tag{2}$$

$$O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_{2(aq)} \quad E^0 = 0.70 \text{ V} \tag{3}$$

$$H_2O_{2(aq)} + h\nu \rightarrow 2 \; {}^{\cdot}OH_{(aq)} \tag{4}$$

$$H_2O_{2(aq)} + Fe^{2+}_{(aq)} \rightarrow {}^{\cdot}OH_{(aq)} + Fe^{3+}_{(aq)} + OH^-_{(aq)} \tag{5}$$

Hydroxyl (${}^{\cdot}OH$, $E^0 = 2.73$ V versus standard hydrogen electrode (SHE)) and sulfate ($SO_4^{\cdot-}$, $E^0 = 2.44$ V versus SHE) radicals, the strongest oxidants known after fluorine, are most often used in EAOPs for

Review article

Table 1 | Contaminants of concern or resources of interest in different water sources and candidate electrified processes

Application	Source water	Contaminants or resources	Conventional processes	Problems and challenges	Electrified processes
Drinking water production	Surface water	Bacteria	Chemical disinfection (Cl_2 and so on)	Disinfectant-resistant pathogens Disinfection by-products	Electrochemical disinfection
	Groundwater	Oxyanions, heavy metals, hardness, trace organics (pharmaceutical and personal care products, per- and polyfluoroalkyl substances and so on)	Adsorption, ion exchange	Slow kinetics High chemical use for regeneration Waste production	CDI, electrodialysis, EAOP, ERP
Wastewater treatment	Municipal wastewater	Nutrients (N and P)	Biological process	Slow kinetics Low stability Sludge production	CDI, electrodialysis, ERP
	Industrial wastewater: brine, leachate, oil and gas, mining, coal chemical process wastewater and so on	Chemical oxygen demand, toxic organic compounds, refractory organic compounds	Biological process	Slow kinetics Low stability Toxicity to bacteria	EAOP, ERP
			Advanced oxidation processes (O_3 and so on)	High energy consumption and cost High chemical consumption	
		Common salts, heavy metals, oxyanions, hardness, scale-forming minerals	Nanofiltration, reverse osmosis	Membrane fouling High energy consumption Lack of selectivity Low water recovery	CDI, electrodialysis, ERP
			Thermal process	High energy consumption Lack of selectivity	
			Ion exchange, adsorption	High chemical consumption Brine production	
Mining and resources recovery	Seawater, surface or underground brines, municipal/industrial wastewater and so on	Li, Au, Ag, rare-earth elements, nutrients, acids, bases	Adsorption, ion exchange Chemical precipitation	Slow kinetics owing to low target contaminant concentration Interference from high concentrations of competing species	Selective CDI, electrodialysis, ERP, EAOP

CDI, capacitive deionization; EAOP, electrochemical advanced oxidation process; ERP, electrochemical reduction process.

water treatment. They react non-selectively with organic compounds in water through hydroxylation, dehydrogenation and charge-transfer reactions, leading to the rupture of aromatic rings, breakage of C–C bonds and eventually to complete mineralization, forming CO_2 and water. The oxidation of some refractory organics (such as per- and polyfluoroalkyl substances, PFASs) may require a potential higher than the redox potential of $^\bullet$OH (Fig. 2a). In this case, direct electron transfer is needed to initiate the oxidation of these organics at higher potential[17].

Electrochemical reduction processes

ERPs utilize reduction reactions on the cathode to transform oxidized pollutants, such as oxyanions (NO_3^-, SeO_4^{2-}, ClO_4^-, BrO_3^-, CrO_4^{2-} and so on), heavy metals (Cu^{2+} and so on) and organic halides, which are very difficult to degrade or remove using conventional methods[21]. Compared with EAOPs, ERPs have been less studied, although they have been attracting increasing interest because of their high efficiency and selectivity for the reduction of toxic species in wastewater[22–27]. In an ERP, electrons can transfer from the cathode material to the reactant directly or indirectly (Fig. 1b). Similar to direct anodic oxidation, direct electrochemical reduction involves contaminant adsorption, then direct electron transfer from the cathode to the target contaminant, followed by desorption of the reduced product. Some well-known direct ERPs used in water treatment include the electrocatalytic reduction of oxyanions (such as NO_3^- (refs. 21,28,29), ClO_4^- and BrO_3^- (refs. 24,30,31)), the dehalogenation of organohalogenated pollutants[32] and the reduction of metals[33–35].

In the aqueous phase, indirect electron transfer usually occurs through the formation of elemental hydrogen ($H^\bullet$)[36–39]. This reductive mediator is formed through the reduction of H^+ from water dissociation, that is, the Volmer reaction, at the cathode surface (equation (6)). $H^\bullet$ produces a strong reducing environment ($E^\circ(H^+/H^\bullet) = -2.31$ V versus SHE) that is highly conducive to the reduction of oxidized pollutants. However, the accumulation of $H^\bullet$ on the cathode surface may lead to the formation of the dihydrogen molecule (H_2) through the Tafel reaction (equation (7)), which decreases the Faradaic efficiency for pollutant reduction and may have other negative impacts such as electrode material embrittlement caused by H_2 accumulation in the
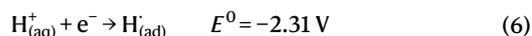
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Box 1

Electrode activity, selectivity and stability

The relative electrochemical reaction rates of different species — target contaminant, water, competing chemicals and the electrode material itself — determine the key performance aspects of an electrode material: activity, selectivity and stability (see the figure).
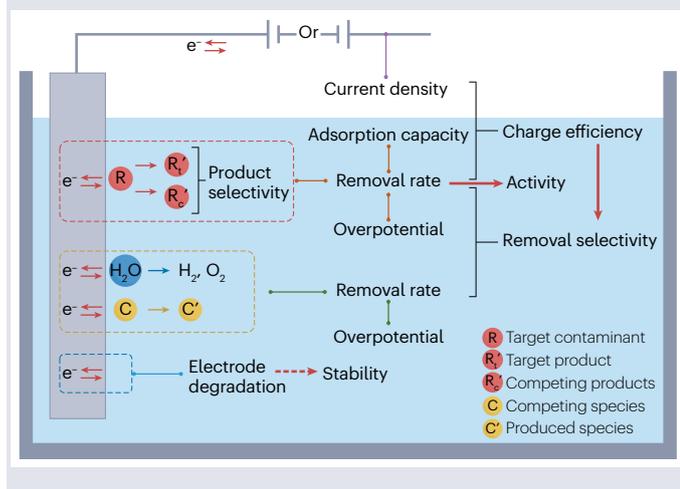
cathode interstices and mineral scaling resulting from the increased local pH. The stability of H• depends strongly on the cathode material. Platinum-group metals (such as Pt, Pd and Rh) are known to stabilize H• on their surfaces and are therefore often used as catalysts for ERPs.

$$H^+_{(aq)} + e^- \rightarrow H^•_{(ad)} \qquad E^0 = -2.31 \text{ V} \qquad (6)$$

$$H^•_{(ad)} + H^•_{(ad)} \rightarrow H_{2(g)} \qquad (7)$$

$$e^- \leftrightarrow e^-_{(aq)} \qquad E^0 = -2.88 \text{ V} \qquad (8)$$

Solvated electrons (e^-) are also reductive mediators with an even lower redox potential ($E° = -2.88$ V versus SHE) (equation (8); Fig. 1), and are believed to be responsible for the reduction of highly refractory species including polychlorinated biphenyls. Other reductive radicals, such as $CO_2^{•-}$, $HS_2^{•-}$, $HO_2^•$ and $I_2^{•-}$ (Fig. 1) may also be formed in ERPs, depending on the composition of the water and wastewater, and react with target pollutants. In addition, radical precursors (such as titanocene[40,41]) can be added to the solution to generate reductive radical intermediators. Reactions at the cathode not only generate reductants for indirect ERPs but can also produce intermediate oxidants. A well-known example is H_2O_2 generation from the oxygen reduction reaction (ORR)[27,42–44], providing a powerful oxidant for water disinfection and contaminant oxidation. This indirect cathodic reaction provides alternative strategies, such as the electro-Fenton process, for water treatment[45].

Electrosorption

Electrosorption refers to the separation of ionic contaminants from water through adsorption of counter ions on the surface of the porous electrodes[46]. A typical electrosorption process cycles between an electrosorption phase, in which ions adsorb on the oppositely charged electrodes to generate a desalinated stream, and a desorption phase, in which adsorbed ions are released and a concentrated brine containing high concentrations of ions is generated[11]. Desorption is triggered by short-circuiting the electrodes or by reversing their polarity. Based on the adsorption mechanism, electrosorption can be classified either as a non-Faradaic process or as a Faradaic charge-transfer process.

In a non-Faradaic process, the electrical charge on the electrode is compensated through the enrichment of counter ions and the depletion of co-ions in the EDL formed on the electrode surface[47] (Fig. 1c). The low voltage imposed (usually below 1.23 V) is not intended to induce interfacial charge transfer, but to drive the electro-migration of charged species as well as to store counter ions in the EDL[48,49]. The adsorption capability of the electrode is determined by its surface area, pore geometry and the applied voltage. However, the low voltage used does limit the electrosorption capacity of non-Faradaic electrodes[50]. Because the electrostatic interaction responsible for ion adsorption is nonspecific, the process also has low selectivity. As a comparison, interfacial charge transfer may also occur upon electrosorption, leading to Faradaic reactions of the ion with the electrode materials. Other than electrostatic ion adsorption on the electrode surface in a non-Faradaic process, Faradaic reactions enable ion adsorption inside the molecular or atomic interstices of an electrode material through electrochemical interactions such as intercalation[47] and redox reactions[10]. As a result, Faradaic charge-transfer processes possess a higher electrosorption capacity, better selectivity towards the target contaminant, higher charge efficiency and a lower dependance on the electrode surface area compared with non-Faradaic processes.

Key electrode characteristics and performance metrics

The performance of an electrified water treatment process is measured by the degradation rate of the target contaminant per unit of electrode mass and the energy efficiency. Together, these two performance metrics determine the amount of electrode material required per unit treatment capacity and the specific energy consumption (SEC in equation (9)). SEC is measured by the amount of energy needed to remove a unit mass of the target contaminant (in joules per milligram or joules per mole), to achieve a single order-of-magnitude decrease in the contaminant concentration (electrical energy per order), or to treat a unit volume of water (in kilowatt hours per cubic metre).

$$\text{SEC} = \frac{\int_0^t UI \, \mathrm{d}t}{Qt(C_0 - C_t)} \text{ or } \text{SEC} = \frac{\int_0^t UI \, \mathrm{d}t}{V(C_0 - C_t)} \qquad (9)$$

Here U is the applied voltage (in volts), I is the current (in amperes), Q and t are the flow rate (in litres per second) and operation time (in seconds), respectively, in continuous-flow operation, V is the solution volution (in litres) when operated in a batch mode, and C_0 and C_t are the contaminant concentrations (in milligrams per litre) before and after the treatment, respectively.

These performance metrics depend on the activity, selectivity and stability of electrode materials, which are further determined by the relative electrochemical reaction rates of different species on the

Review article

electrode surface: the target contaminant, water, other chemicals in the water and the electrode material itself (Box 1). Specifically, the electrode activity towards a target contaminant is directly measured by the reaction/removal rate (RR) of the target species (equation (10)) within a period of time:

$$RR = \frac{C_0 - C_t}{C_0} \qquad (10)$$

Besides RR, the overpotential η – which is the difference between a half-reaction's thermodynamic redox potential and the potential at which the redox event experimentally occurs with a certain reaction intensity – is sometimes used as an indirect measure of electrode activity in EAOPs and ERPs. A low overpotential suggests high activity towards the reaction of interest and vice versa. We note that the overpotential varies with the solution chemistry and the selected current density. Therefore, the solution chemistry and current density should be reported when comparing the overpotential of different materials for a specific reaction.

The selectivity of an electrode is defined by the rate of target contaminant degradation relative to side reactions that do not contribute to the removal of the target contaminant, that is, the removal selectivity, or the rate of target product formation relative to that of undesired by-products; that is, the product selectivity (Box 1). A high selectivity

towards harmful contaminants or valuable resources has obvious energetic, environmental and economic benefits[51,52]. The binary selectivity coefficient ($S_{T/C}$) between a target (T) and a competing (C) species, also sometimes referred to as the separation factor, is defined by equation (11)[53–55].

$$S_{T/C} = \frac{(C_{T0} - C_{Tt})/C_{T0}}{(C_{C0} - C_{Ct})/C_{C0}} \qquad (11)$$

Here, C_{T0}, C_{Tt}, C_{C0}, C_{Ct} are the concentration of target species (subscript T) and competing species (subscript C) before and after the treatment, respectively. In direct electrochemical oxidation or reduction processes, the selectivity depends on the affinity of the target compound to the electrode material; in indirect oxidation or reduction, the reactivity of the target compound towards the oxidative or reductive radicals relative to that of the competing species also affects the selectivity.

The selectivity in a complex system with more than one side reaction (such as with water, competing species and the electrode itself; see Box 1) is better measured by the charge efficiency, also called the current efficiency, the Coulombic efficiency or the Faradaic efficiency in different systems. Charge efficiency is defined as the percentage of the invested electrical charge used for the target contaminant removal (equation (12)).
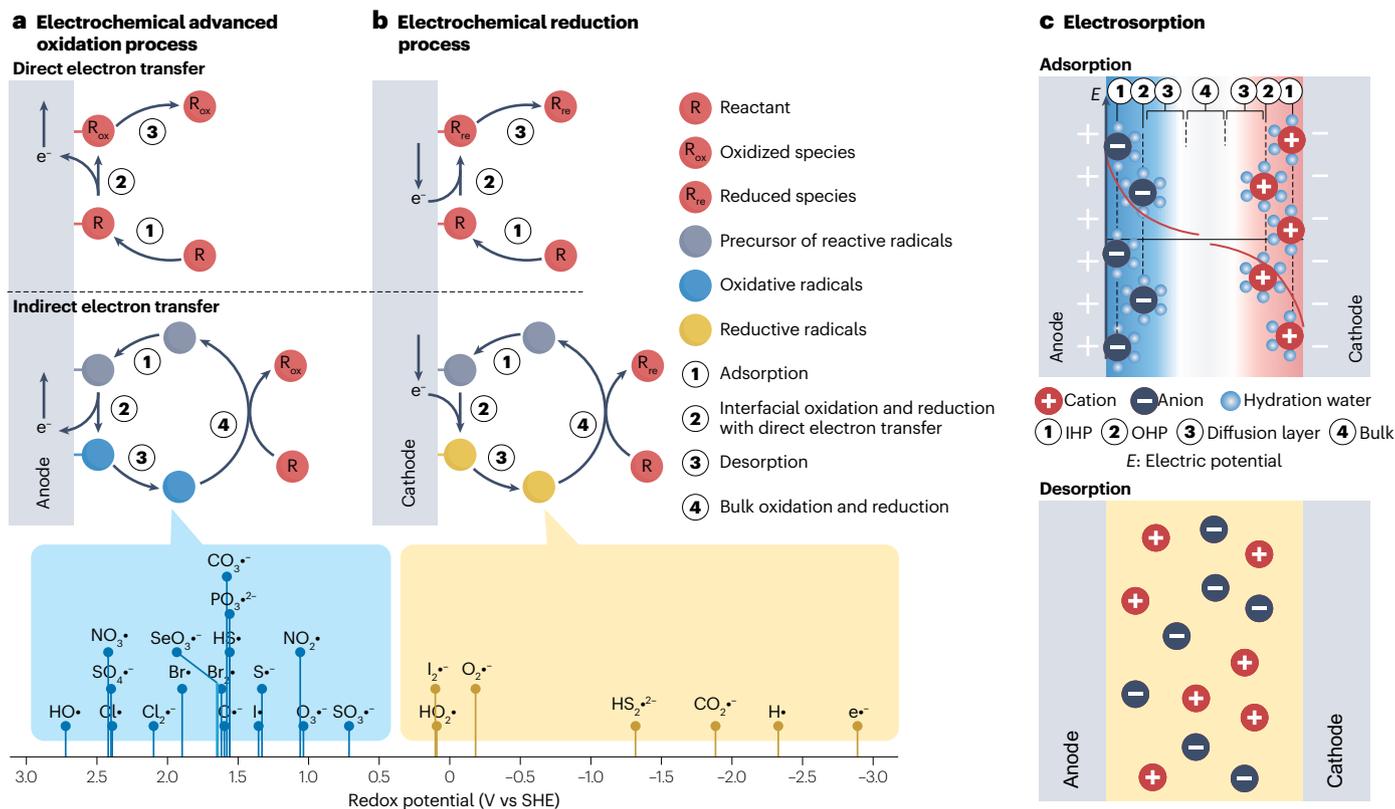
Fig. 1 | Principles of the main electrified processes for water and wastewater treatment. a,b, Direct and indirect electron transfer process in electrochemical advanced oxidation processes (**a**) and electrochemical reduction processes (**b**). Redox potential values of the radicals are obtained from ref. 18; these values are for their most common redox pairs. **c,** Adsorption and desorption processes in electrosorption. IHP, inner Helmholtz plane, which passes through the centres

of the ions that lose some of their hydration water molecules and are directly adsorbed on the electrode surface. OHP, outer Helmholtz plane, which passes through the centres of solvated ions at the distance of their closest approach to the electrode. The diffusion layer is the region beyond the OHP where the concentrations are different from their value in the bulk solution. SHE, standard hydrogen electrode.

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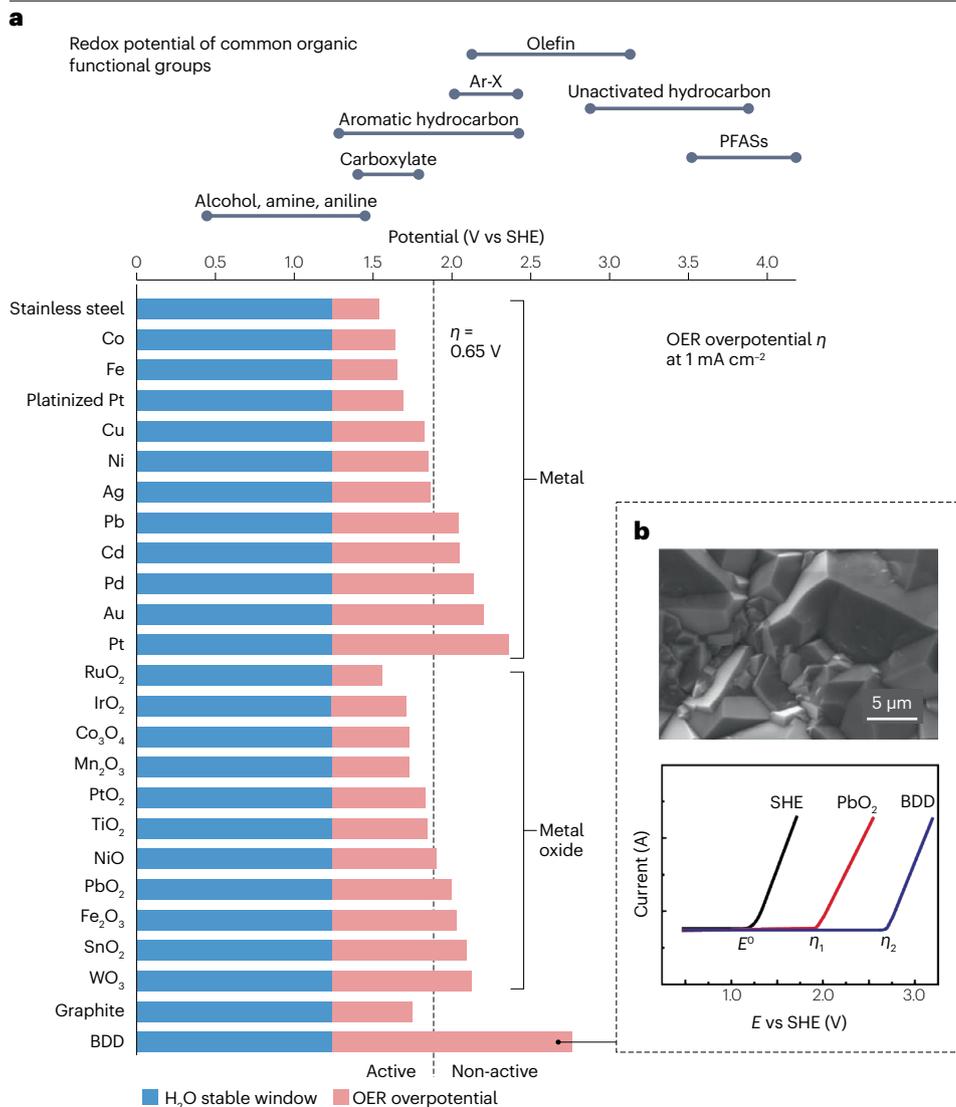
Fig. 2 | Common organic contaminants and anode catalytic materials. a, Redox potential of common organic contaminants and the oxygen evolution reaction (OER) overpotential η of common electrode materials at a current density of 1 mA cm^{-2}. The redox potential of common organic contaminants is obtained from refs. [17,70]. The OER overpotential data were obtained from ref. [71] except for TiO$_2$ (ref. [72]), PbO$_2$ (ref. [73]) and SnO$_2$ (ref. [74]). **b**, The scanning electron microscope morphology of the boron-doped diamond (BDD) electrode (top) and the theoretical current–potential curve of BDD and PbO$_2$ for the OER (bottom). PFASs, per- and polyfluoroalkyl substances; SHE, standard hydrogen electrode. Scanning electron microscope image in panel **b** adapted with permission from ref. [235], Elsevier.

$$\text{CE} = \frac{FnQ(C_0 - C_t)}{MI} \text{ or } \text{CE} = \frac{FnV(C_0 - C_t)}{MIt} \qquad (12)$$

Here, F is the Faraday constant (96,485 C mol^{-1}), n is the number of electrons transferred to convert the target contaminant to the final product and M is the molar mass of the target compound.

The electrode stability can be defined by an electrochemical window[56], which is an electric potential range in which the electrode is neither chemically oxidized or reduced nor physically damaged (cracking, exfoliation, swelling, shrinking and so on). Electrode stability can be substantially reduced when operating at a potential beyond the electrochemical window or in harsh conditions, such as extreme temperature, salinity or pH[56]. Electrode stability can also be affected by organic fouling or inorganic scaling, which are normally reversible; the electrode performance can be recovered using cleaning protocols.

The performance of an electrified process is intrinsically determined by the properties of the electrode material. The key physicochemical characteristics of an electrode include electric conductivity,

specific surface area and surface chemistry. The electric conductivity of the electrode affects the overall resistance of the electrified system. Low conductivities may result in higher cell potentials for a given condition of applied current density. Specific surface area defines the effective area and number of reaction sites for electrified processes and is therefore proportionally related to the degradation or electrosorption kinetics. Surface chemistry dictates the affinity for the target compound relative to other chemical species, such as water and competing compounds, and is therefore closely related to the electrode's catalytic activity and selectivity. Understanding the interfacial processes involved in electrochemical reactions is key to better design and fabrication of electrodes. Advanced electrode characterization techniques that probe reactions and interfacial processes in situ and in operando are revolutionizing the electrochemistry research landscape. Scanning electrochemical microscopy maps electrocatalytic responses of electrodes at the micro- and nanometre scale and allows the identification of high performance regions that can be correlated with imaging and spectroscopic material characterizations[57–59].

Review article

Combination of electroanalytical methods with in operando spectroscopy (such as IR[60,61], Raman[62,63], UV-vis[64,65] or mass spectroscopy[66]) provides complimentary information regarding the electrode–electrolyte interface and allows the monitoring of the target molecule's changes induced by direct or indirect electrochemical reactions at the electrode.

Electrode materials for electrified water and wastewater treatment

Developing low-cost, high-performance electrode materials that have high activity, selectivity and stability is critical to sustainable water supply. The performance of different electrode materials for water treatment has been investigated in a number of studies[47,67–69]. In EAOPs and ERPs, high-performing electrodes should have low overpotential for the target pollutant but high overpotential for side reactions in order to minimize the impact of side reactions on the efficiency of target pollutant degradation. In electrosorption, however, electrodes with high accessible surface area and ion diffusion rates are desired. Increasing research focuses on improving the selectivity of the electrode, which plays a major part in the overall energy efficiency of the process.
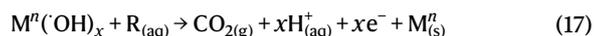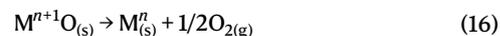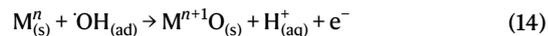
Anode materials

Common organic pollutants found in water and wastewater include alcohols, amines, carboxylates, aryl halides (Ar–X), aromatic hydrocarbons, olefins and unactivated hydrocarbon ($C(sp^2)$–H)). Figure 2a shows their standard redox potentials[17,70]. The oxidation of organic substrates with low redox potentials (such as alcohols) can be achieved through direct electron transfer on the anode surface, whereas direct electrolysis of organic pollutants with high redox potential (such as olefins, unactivated hydrocarbons and PFASs) is more challenging because the potential required is higher than that for the oxygen evolution reaction (OER, redox potential of 1.23 V versus SHE; equation (13)). Therefore, an electrode material needs to have a high OER overpotential (η) to avoid oxygen production in order to promote the direct electrochemical oxidation of organic pollutants, or to generate oxidative radicals (such as $\cdot$OH with redox potential of 2.73 V versus SHE; equation (1)) for indirect oxidation.

The OER overpotential is largely determined by the electrode material's affinity to $\cdot$OH, which reacts with the electrode to generate oxygen. Figure 2a shows the OER overpotential of some electrode/electrocatalyst materials relative to the theoretical redox potential of OER (1.23 V versus SHE)[71–74].

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \quad E^0 = 1.23 \text{ V} \tag{13}$$
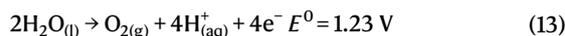
Anode materials are considered 'active' or 'non-active' based on their susceptibility to redox reactions with $\cdot$OH during electrochemical processes[75]. Active anode materials have high enthalpy of $\cdot$OH adsorption. Therefore, electrogenerated $\cdot$OH chemisorbs strongly to and reacts quickly with active anode materials (such as metals and metal oxides), leading to their oxidation (equation (14)). The oxidized electrode material can then oxidize the contaminants (R) through an oxygen transfer reaction (equation (15)) or form dioxygen (equation (16)), which restores the surface site to its original oxidation state (M^n). These reactions lead to a low concentration of $\cdot$OH on an active anode surface, which is often insufficient to mineralize the recalcitrant organic compounds in water, but can lead to more biodegradable intermediates. Electrode materials that exemplify this characteristic behaviour are platinum-group metals and dimensional stable anodes, consisting of metal oxides and mixed metal oxides (such as RuO_2, IrO_2, RuO_2–TiO_2 and IrO_2–Ta_2O_5).

$$M^n_{(s)} + \cdot OH_{(ad)} \rightarrow M^{n+1}O_{(s)} + H^+_{(aq)} + e^- \tag{14}$$

$$M^{n+1}O_{(s)} + R_{(aq)} \rightarrow M^n_{(s)} + RO_{(aq)} \tag{15}$$

$$M^{n+1}O_{(s)} \rightarrow M^n_{(s)} + 1/2O_{2(g)} \tag{16}$$

$$M^n(\cdot OH)_x + R_{(aq)} \rightarrow CO_{2(g)} + xH^+_{(aq)} + xe^- + M^n_{(s)} \tag{17}$$

Non-active anodes have high overpotential of OER and low $\cdot$OH adsorption enthalpy. These electrodes physisorb $\cdot$OH weakly, allowing the mineralization of organic compounds that reach the electrode surface (equation (17)). Well-known non-active anode materials include PbO_2, SnO_2, the Magnéli phases of TiO_2 and boron-doped diamond (BDD).

BDD is considered the gold standard for anode materials used in EAOPs (Fig. 2b). In BDD, the boron atom substituting for carbon in the diamond lattice consumes an extra electron for chemical bonding and creates an excess hole, resulting in a p-type semiconductor[76]. The electric conductivity of BDD increases substantially with the concentration of boron dopant, from semiconducting to <0.1 Ω cm when the B doping level increases from 10^{17} to 10^{20} atoms cm^{-3} (ref. 77). BDD lacks 'binding sites' to mediate electron transfer between its surface and a water or solute molecule[78], so it has a wide potential window of stability in aqueous media, and has minimum electrode poisoning. These characteristics have not been observed in other non-active electrodes.

Because of the high cost of BDD electrodes, much research has been devoted to discovering lower-cost materials that can compete with BDD electrodes in performance. Doping is often used to improve the performance of metal oxides. For example, Sb doping can increase the electric conductivity and OER overpotential of SnO_2 (refs. 74,79). Doping Fe, Co, Bi, F and rare-earth oxides into PbO_2 can decrease its crystal grain size and increase its electrochemical activity[80]. Ceramic Magnéli-phase Ti_4O_7 (trade name Ebonex)[81] and Nb-doped rutile TiO_2 (ref. 82) are highly conductive ceramic materials that produce large quantities of $\cdot$OH and hence exhibit better performance in water treatment. However, these materials suffer from low stability, resulting in a short lifetime and slow leaching of toxic metals (such as Pb and Sb), which has limited their commercial application.

In general, anodic materials with $\eta > 0.65$ V are considered to be non-active[83,84]. However, it is important to note that electrode materials or electrocatalysts do not behave exclusively as active or non-active. Furthermore, an electrode material's activity towards $\cdot$OH can be tuned through compositional and structural changes. For example, increasing the carbon sp^2/sp^3 ratio in the BDD crystalline structure can narrow the electrochemical window of BDD to yield onset potentials of OER closer to thermodynamic values for glassy carbon electrodes. Such BDD electrodes with high sp^2 impurities can exhibit behaviours close to those of active electrodes[78]. Conversely, the reductive treatment of TiO_2 to form Magnéli-phase titanium oxide can increase η up to that of BDD. Therefore, expanding the narrow catalogue of stable anodes for EAOPs by electrode engineering is possible. Understanding electrode stability and mechanisms of ageing and failure could guide research efforts to develop electrode materials with a higher η and sustained performance, competitive with BDD.

Review article

EAOPs can attain complete mineralization of contaminants to CO_2 when given enough contact time, during which strong oxidants are continuously electrogenerated in non-active anodes. The oxidation of aromatic compounds tends to yield short-chain carboxylic acids that are non-toxic and can easily be biodegraded or even photolysed[7]. However, incomplete mineralization may result in organic by-products affecting the effluent toxicity. In some instances, generated by-products may be even more toxic than the original pollutant. Unfortunately, because most studies in the literature focus on the abatement of total organic carbon (that is, mineralization), very few studies have assessed product toxicity resulting from incomplete treatments. Further attention should be given to investigating reaction pathways in order to understand changes in reaction products and the associated toxicity over treatment time by EAOPs[85,86]. Another important aspect to consider is the toxicity induced by the generation of undesired inorganic species from reactions of electrolyte ions in water. For example, chloride, a ubiquitous ion in natural water and wastewaters, can form chlorate and perchlorate under highly oxidizing conditions with non-active electrodes. Active electrodes, on the other hand, tend to form free chlorine species, which can be used for disinfection of water (that is, electrochlorination), but may also result in the formation of disinfection by-products when reacting with organic compounds in water[87–89]. Strategies to minimize the impact of undesired by-products may involve simultaneous electrochemical degradation of the by-products (such as electrocatalytic dehalogenation by cathodic reactions) or post-treatments (such as adsorption) to remove toxic by-products.

Cathode materials

Because cathodic polarization generally does not induce corrosion of the electrode, a wider range of materials can be used as the cathode. Research on cathode materials has focused on energy efficiency and selectivity towards the target pollutants. Figure 3a shows some well-known ERPs used in water treatment, including oxyanion reduction, H_2O_2 production through cathodic ORR, dehalogenation and heavy metal removal, and the thermodynamic potentials of the redox pairs involved. Because H_2O is undoubtedly the most abundant species in wastewater with concentrations many orders of magnitude higher than the target contaminants, the efficiency of many ERPs is hindered by the hydrogen evolution reaction (HER) that occurs at a thermodynamic potential of 0 V versus SHE (equation (18)). Therefore, designing proper cathode catalysts to increase the HER overpotential is critical to improving the selectivity and energy efficiency of the cathode material towards degradation of target pollutants.

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \quad E^0 = 0\ V \tag{18}$$

Oxyanion reduction. Oxyanions (such as NO_3^-, ClO_4^-, BrO_3^- or SeO_4^{2-}) are common pollutants in both natural water and wastewaters. As NO_3^- is one of the most widespread pollutants, research on removal of NO_3^- by ERPs has seen an upsurge. NO_3^- can go through a five-electron transfer pathway to form N_2, an ideal degradation product, although forming the N≡N triple bond is very challenging and currently reported charge efficiencies are still quite low. On the other hand, an eight-electron reduction pathway can generate NH_3 as a chemical or hydrogen energy carrier. Copper (Cu) is one of the most frequently reported catalysts for eight-electron NO_3^- reduction, as it can suppress HER better than most other transition metals[90–97] (Fig. 3a,b). Some Ti-based materials also show good selectivity for NO_3^- reduction for a similar

reason[98,99]. Nevertheless, both Cu and Ti also have high overpotential for the NO_3^- reduction reaction. To address this, researchers have developed metal alloy and single-atom catalysts, where Cu is used as the substrate to suppress HER, and another active metal (such as Co, Ni, Fe, Ru and so on), serves as the active NO_3^- reduction site[92–95,100–102] (Fig. 3c). This approach has demonstrated a Faradaic efficiency close to 100% and a current density as high as 1 A cm^{-2}. These studies also suggest that proper selection of metal elements in bimetallic or multi-metallic catalysts can help to optimize energy barriers in multi-electron-transfer reactions. Accordingly, tuning the atomic (such as metal alloy arrays, clusters or single-atom) and electronic structure (such as oxidation states of the active sites) can be important strategies for developing highly active electrocatalysts.

Limited work has been done on ERPs for the removal of other oxyanions such as ClO_4^- and BrO_3^- (refs. 24,30,31). Monometallic catalysts including Pt[103], Rh[104], Zn[105], Cd[106], Cr[106], Cu, Ru, Mo and Pd have been shown to electrochemically reduce ClO_4^-, following the order of Rh > Cu > Ru > Mo > Pd[107]. A Rh–Cu bimetallic catalyst achieved effective ClO_4^- reduction without forming unwanted biproducts (ClO_3^-, ClO_2^- and ClO^-)[107]. Bimetallic catalysts[108] and metal–carbon composites[109] have also been used for electrochemical reduction of BrO_3^-, with Pd-based catalysts showing outstanding performance. These studies demonstrated the potential of efficient electrochemical reduction of oxyanions for water treatment, but also pointed out the need for greater reaction rate, greater stability and the ability to treat low concentrations of pollutants as critical future challenges[108,109].

H_2O_2 production using cathodic ORR. Cathodic two-electron ORR is an environmentally friendly method for the on-site generation of H_2O_2 (refs. 42–44), an important reagent used in advanced oxidation processes. A Hg–Au alloy was the first reported catalyst with substantial H_2O_2 generation[110]; other noble-metal catalysts were later reported to show low ORR overpotentials and much higher selectivity (up to 98%), including Pd–Hg, Ag–Hg[111], Pt–Hg, Cu–Hg[112] and Pd–Au[113] alloys and Au–Ni–Pt core–shell nanorods[114]. Single-atom catalysts (Mo-based[115] and Pt-based[116,117], Fe–C–O[118] or Co–N–C[119]) have high activity and selectivity (>90%) for H_2O_2 production (Fig. 3d). Modified-carbon catalysts prepared by surface oxidation (such as graphene oxide and oxidized carbon nanotube, CNT)[26,120–122], or by doping heteroatoms such as B[123,124], N[125–127], P[115] or F[128] to tune their electronic structures, have also emerged as effective materials to generate H_2O_2 on-site. These strategies demonstrate that using low-cost carbon-based catalysts as active cathode materials is possible. Future studies need to address the scaling-up of electrode fabrication and stability of catalysts under different solution conditions (such as harsh pH or a high concentration of impurities). In addition, the configuration of the electrode or reactor to accommodate a gas (oxygen)–liquid (water)–solid (catalyst) three-phase interface also requires more attention, because it determines the mass and charge transport and directly affects the reaction kinetics.

Dehalogenation. Electroreduction is an effective method of dehalogenation as it can facilitate the cleavage of recalcitrant organic halides including PFASs[129], trichloroethylene[130], chloroacetic acid[131] and hexachlorocyclohexane[132]. Ag catalysts are among the best for organic halide reduction[133], because they can reduce different C–X bonds through direct electron-transfer processes[131,132,134]. Alternatively, a well-known mechanism for the indirect reduction of organic halides is through the production of atomic hydrogen as the reductant[36,37]. In this case, the most widely used catalyst is Pd, because Pd has great
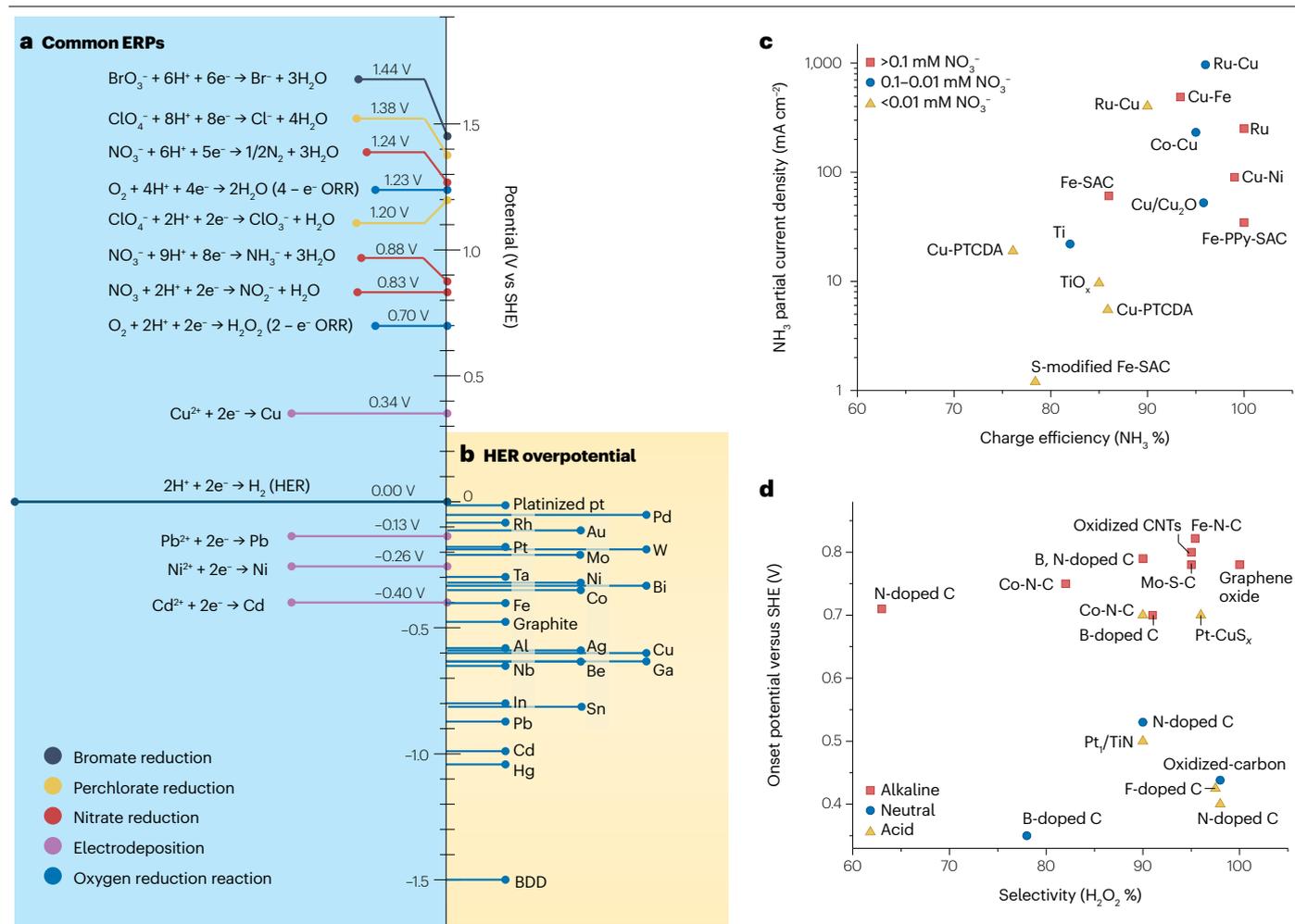
Fig. 3 | Common ERP reactions and typical materials utilized for ERPs in water treatment. a, Electrochemical reduction potential of common reactions in electrochemical reduction processes (ERPs). **b**, Hydrogen evolution reaction (HER) overpotential of common metals. Data were obtained from ref. 71. **c**, Reported materials for NH_3 generation via NO_3^- reduction and their performance. Data used in the figure can be seen in Supplementary Table 1.

d, Reported anode materials for H_2O_2 production via two-electron oxygen reduction reaction (ORR) and their performance at different solution pH. Data used in the figure can be seen in Supplementary Table 2. BDD, boron-doped diamond; CNT, carbon nanotube; PPy, polypyrrole; PTCDA, 3,4,9,10-perylenetetracarboxylic dianhydride; SAC, single atom catalyst; SHE, standard hydrogen electrode.

affinity for hydrogen atoms[135]. Catalysts that enhance HER (such as TiN and MnO_2) can be added onto Pd to increase the production of hydrogen atoms, which then adsorb on Pd to cleave the R–X bond in organic halides[131,136–138]. Besides atomic hydrogen, hydrated electrons (−2.88 V versus SHE) can be generated by ultraviolet-assisted processes and used for indirect ERPs. A recent study coupled ultraviolet light with electroreduction to generate hydrated electrons using surfactant-modified CNT as the cathode, and enhanced PFAS removal[129]. However, a better mechanistic understanding of direct or indirect electro-reduction of halogenated organic compounds is needed to improve electrocatalyst design[139].

Heavy-metal removal. Heavy-metal removal by electrodeposition is a direct ERP. Unlike other ERPs discussed above, electrodeposition reactions do not depend strongly on the electrode's chemical composition because most electrodes have low overpotential for electrodeposition.

Therefore, most electrodeposition reactions are sensitive only to the reduction potential of the metals to be reduced. Common electrode materials used for electrodeposition include stainless steel and carbon-based materials[140,141]. Design of these electrodes focuses on the micro- or macro- structure, cost and abundance of the material[34].

In both EAOPs and ERPs, selection of the counter-electrode is also very important, as the interplay of the anode and cathode reactions may negatively affect the degradation of the target compound. The counter electrode needs to be low cost, produce no unwanted substances, and have low overpotential in order to decrease the energy consumption. In addition, the design of the electrochemical reactor (for example, undivided versus divided cells) must be carefully considered to avoid interference from reactions on the counter electrode. In an undivided cell, both oxidation and reduction reactions occur in the same chamber with the possibility of desired reaction products being re-oxidized or re-reduced on the counter electrode. A divided cell
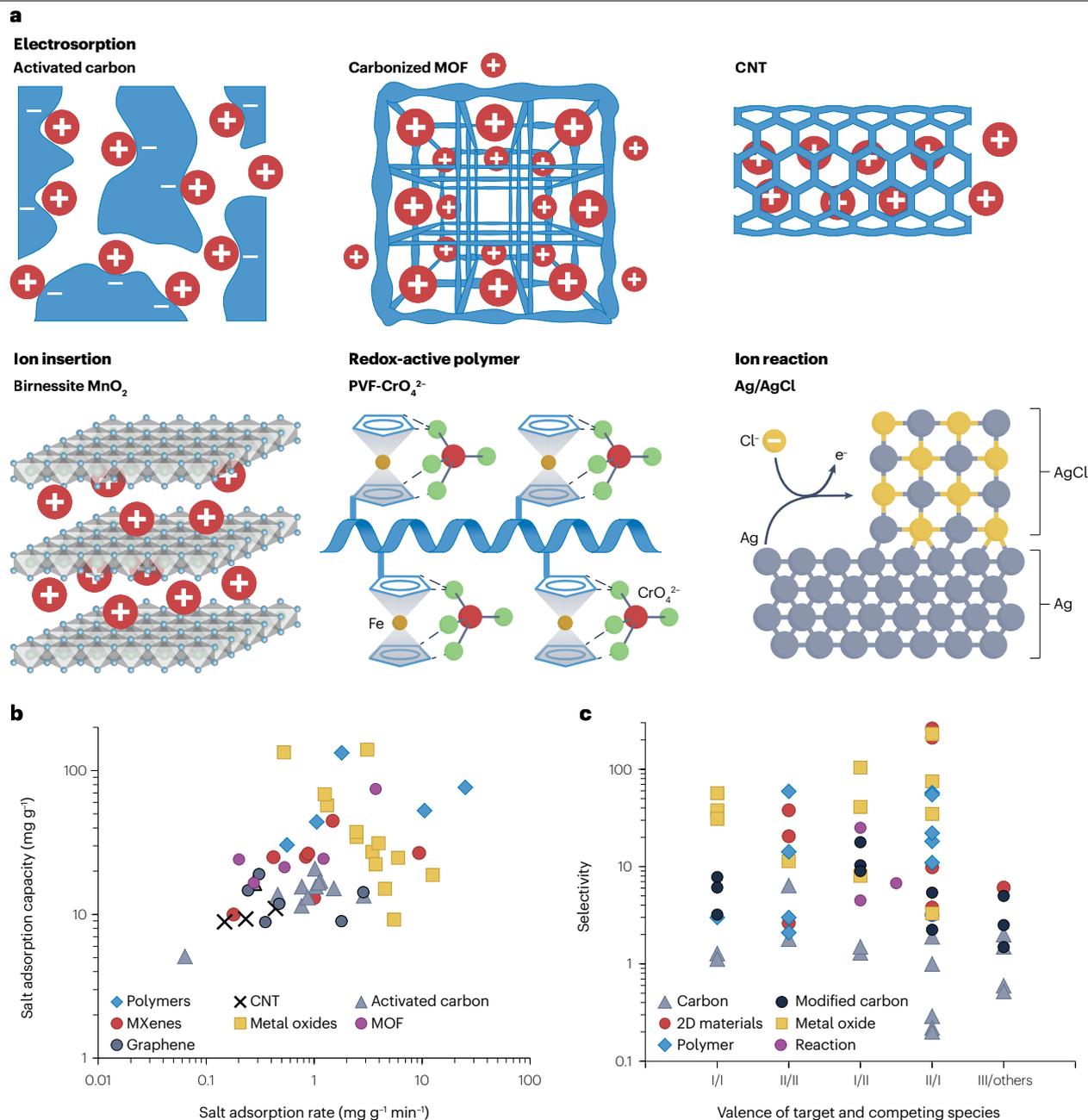
Fig. 4 | Typical processes, materials and performance for electrosorption of ions. a, Typical processes and materials for ion electrosorption. **b**, Ion adsorption capacity and rate of various electrode materials. Data used in the figure are in Supplementary Table 3. **c**, Selectivity coefficients reported in separation of target ions from competing ions of different valences (I, II, III represent the charge number of different species in water). Data used in the figure are in Supplementary Table 4. CNT, carbon nanotube; MOF, metal–organic framework; MXenes, metal carbides, nitrides and carbonitrides; PVF, poly(vinyl)ferrocene.

design avoids this problem at the expense of higher system resistance and therefore higher energy consumption.

Electrosorption electrodes

Electrosorption processes were first reported over 60 years ago[142]. However, research only substantially picked up after carbon aerogel materials began to be used; these have both very high specific surface area and high conductivity, showing a breakthrough in electrosorption performance[46,143]. The material properties of the electrode — including surface area, porosity and pore size distribution, electric conductivity, capacitance, hydrophilicity and stability — are key factors influencing electrosorption efficiency. A good number of studies have reported the performance of different electrosorption materials[11,12,47] (Fig. 4).

Review article

Various forms of carbon, including activated carbon, carbon black, carbon aerogel, CNTs and graphene, have been used as electrode materials for electrosorption. Of these materials, activated carbon is the most studied because of its very high surface area (>2,000 m^2 g^{-1}), suitable pore size distribution (median pore diameter of 1–5 nm), commercial availability and low cost. Activated carbon electrodes have demonstrated an electrosorption capacity of >20 mg of NaCl per gram of electrode[144] (Fig. 4b) and negligible performance decline over long-term operation[145]. They are currently the only electrodes used in commercial capacitive deionization systems. A binder is usually needed to fabricate electrodes using granular, powder or nanoparticulate carbon materials. Carbon cloth, sheets, brushes or felts, however, can be directly utilized as electrodes, and are available in large sizes[146]. However, they usually have lower adsorption capacity than activated carbon. Although graphene has a specific surface area and salt adsorption capacity comparable to that of activated carbon[147–149] (Fig. 4b), its high cost has hindered its application. CNTs have lower specific surface area (normally <1,000 m^2 g^{-1}) than graphene and activated carbon, and hence a lower adsorption capacity (normally <10 mg of NaCl per gram of electrode)[150,151] (Fig. 4b); these characteristics, in combination with their higher cost, make CNTs less attractive. Nonetheless, CNTs and graphene have high electric conductivity and unique one-dimensional or two-dimensional nanostructures with atomic-level surface smoothness, which endows them with great potential for fundamental mechanistic research on ion–electrode interactions, such as ion transport, adsorption and desorption behaviours. Various modifications of carbon materials improve electrosorption performance[51,54,55]. In particular, nitrogen doping improves the electrode conductivity, wettability and affinity to specific ions, increasing the salt adsorption capacity from 17% to 137%[152–155]. Nitrogen functional groups also have selectivity for different ions. For example, pyridinic nitrogen groups tend to capture 'hard' ions (H$^+$ and Na$^+$) but pyrrolic nitrogen groups show selective adsorption of 'soft' ions (Pb^{2+}). Functionalization with guanidinium[156] and aryl diazonium[157] provides a high affinity to phosphate and Sr^{2+}, respectively (Fig. 4c).

Increasingly, highly selective sorbents such as metal–organic frameworks (MOFs) are used in electrodes for selective electrosorption. However, most MOFs are not electrically conducting. Carbonization is therefore carried out to improve the conductivity of MOFs while preserving the uniform porous structure. The reported salt adsorption capacity of carbonized MOF ranges from >20 mg g^{-1} to 167.4 mg g^{-1} (refs. [158–162]) (Fig. 4b), which is much higher than for conventional carbon materials. Some MOFs are, however, electrically conducting, and can potentially be utilized directly for electrosorption. The use of MOFs for electrosorption is a great advance because their subnanoscale pore structure, in combination with the large variety of chemical functionality, provides ample opportunities to develop electrodes with high selectivity[53], which is difficult to achieve using conventional carbon materials.

Compared with the non-Faradaic materials discussed above, charge-transfer materials offer a much higher electrosorption capacity and selectivity owing to their unique charge and ion storage mechanisms (Fig. 4). Ion insertion (or intercalation) materials, including metal oxides (such as the manganese oxide family[163–166]), metal carbides, nitrides and carbonitrides (MXenes) (such as Ti$_3$C$_2$T$_x$ (ref. [167])), and transition-metal dichalcogenides (such as MoS$_2$ (refs. [168,169])), are the most studied charge-transfer materials for electrosorption. They are usually crystalline and highly ordered (Fig. 4a), and possess one-, two- or three-dimensional subnanometre interstitials for ion diffusion and storage. Because of the large number, tunable size and unique subnanostructure of the crystalline interstitial sites, ion insertion materials show not only a notably higher electrosorption capacity than carbon-based materials (Fig. 4b), but also greater selectivity among ions of similar charge (Fig. 4c).

Conductive and redox-active polymers such as poly(vinyl)ferrocene, polypyrrole and polyaniline have also been used in electrosorption owing to the high affinity of their functional groups (ferrocene, amine) towards certain target ions (Fig. 4a). Poly(vinyl)ferrocene has strong affinity towards oxyanions such as sulfonates[170], chromate[10] and arsenate[171], reaching electrosorption capacity >100 mg g^{-1} (ref. [10]) and selectivity coefficient >50 for arsenic over competing anions such as Cl$^-$ and SO$_4^{2-}$ (ref. [171]). Functionalized polypyrrole and polyaniline has achieved selective electrosorption of both target cations (Hg^{2+} and so on[172]) and anions (F$^-$, NO$_3^-$, Cl$^-$ and so on[173,174]) (Fig. 4b,c). Redox couples (such as Ag/AgCl[175] and Bi/BiOCl[176]) have also been utilized as electrodes. These reactive materials exhibit high ion capture capacity through electrochemical reactions and have high selectivity for Cl$^-$ (Fig. 4a).

## Critical challenges in electrified water treatment

Despite their great potential, current electrified water treatment processes face a myriad of challenges, such as the scalable fabrication of electrodes with high porosity, large surface area and stable catalytic coatings, the design of electrochemical reactors with fast mass transport, the interference of competing species, and the fouling and scaling of the electrode. The cost of many high-performance materials (such as BDD, Nb, W, Ta) is still too high for their broad application in water and wastewater treatment. Some critical challenges are further discussed below.

Mass transfer limitations

An important factor affecting electrochemical reaction kinetics is the transport of the target compound to the electrode surface, where electrochemical reactions occur. In many reactors, especially those using the conventional flow-by configuration (that is, contaminant-laden water flows tangentially along the electrode surface), mass transfer can become the rate-limiting step. The role of mass transfer is aggravated at lower contaminant concentrations and higher current density. Given that the concentrations of trace contaminants (such as PFAS or heavy metals) in most water and wastewaters are often at the level of nanograms-to-micrograms per litre, mass transfer limitation may occur even at a moderate current density (5–10 mA cm^{-2})[177]. In a flow-by configuration, the concentration boundary layer can reach about 100 μm (ref. [14]), larger than the dimension of the electrode roughness, and could therefore lower the electrode activity despite a large surface area. As a result, the slow mass transfer not only decreases contaminant removal rate, but also increases overpotential, causing increased energy consumption, aggravated electrode corrosion and intensified side reactions. In addition, the slow mass transfer of reaction products leads to accumulation on the electrode surface, which may result in aggravated organic fouling, inorganic scaling and chemical corrosion of the electrode.

Interference from the complex water matrix

In natural and waste waters, concentrations of competing species (such as Cl$^-$ or NOM) in the water matrix are often orders of magnitude higher than those of target contaminants. These competing species can not only strongly interfere with reactions of the target contaminants but
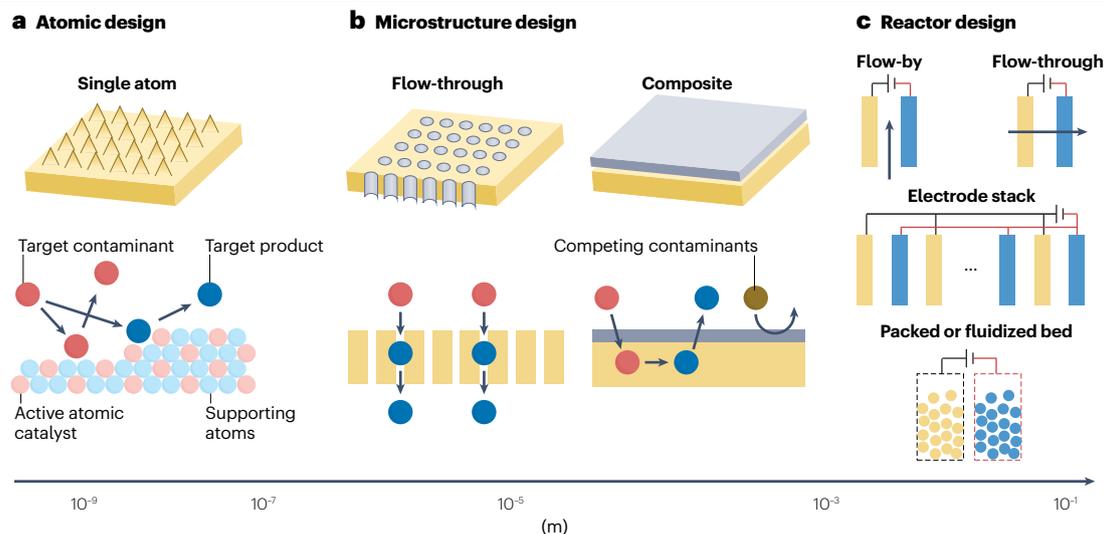
Fig. 5 | Rational electrode design from atomic to device scale. a, Atomic design to improve the material intrinsic activity and selectivity. **b**, Microstructure design to improve mass and charge transfer. **c**, Reactor design to optimize performance for specific applications.

may also generate by-products that are toxic or detrimental to electrodes. As a result, they often dictate the design, operation and energy consumption of the treatment system. Notably, electrochemical oxidation of chloride ions produces reactive chlorine species (such as Cl_2 or $HOCl/OCl^-$) that can be used for disinfection, but they are also strong oxidants that may cause corrosion of electrodes. This process can also generate toxic halogenated organic compounds and other toxic oxidants (such as ClO_4^-)[3,178]. For contaminants that are degraded by direct electron-transfer reactions, such as PFASs, their degradation can be hindered by electrode fouling caused by the adsorption of NOM[17]. Precipitation of metals from the reduction of metal ions in water (such as Cu^{2+} or Fe^{2+}) can block catalysts on the cathode, and thereby hinder the reductive degradation of oxyanions (such as NO_3^- or SeO_4^{2-}).

Degradation of electrode materials
The stability of electrode materials against degradation remains a critical challenge. Despite the superior properties of carbon materials, the very low potential of carbon oxidation (0.207 V versus SHE) makes them highly susceptible to oxidative degradation even in low-potential applications such as capacitive deionization. The high anode potential necessary for oxidation of refractory contaminants, often >3.0 V versus SHE (Fig. 2a), poses an even greater challenge. Mixed metal oxides are commonly used as anode materials with high efficiency for organics degradation, but many mixed metal oxides are not sufficiently stable under the high anodic potential necessary to degrade refractory compounds[179]. Any factors that require increasing operational voltage, such as low water conductivity and high overpotential due to limited mass transfer, could further aggravate the degradation of the electrode material.

Most materials are stable at cathodic potentials, although some metals (such as steel and Ti) may not be suitable as a cathode when hydrogen evolution occurs because of their susceptibility to hydrogen embrittlement accompanied by large volume increases[180]. Furthermore, polarity reversal is often used to remove mineral scales (such as $CaCO_3$) formed on the cathode, when the cathode is subject to an anodic potential and vice versa[181]. Therefore, electrodes must be both cathodically and anodically stable.

Design and development of advanced electrode materials
The rational design of an electrode requires the consideration of materials structure and properties from atomic to device scale (Fig. 5a–c). Specifically, the atomic structure of the catalyst determines the intrinsic catalytic activity and selectivity for target contaminant removal. At the microscopic scale, the distribution of catalysts on the substrate, as well as the binder and current collector used, greatly affects surface area, porosity, electric conductivity and the hydrophilicity of the electrode, which have important roles in charge and mass transfer. At the reactor level, macroscopic electrode design must accommodate the reactor configuration (such as stacked multi-pair electrodes with a flow-by versus flow-through configuration, particulate or granule electrodes in packed or fluidized bed reactors) and operation mode[182].

Computational methods to aid electrode material screening and design
Electrode design for specific electrified applications has traditionally been done by trial-and-error, following educated and inspired guesses. An emerging trend is the use of computational tools such as density functional theory (DFT), microkinetic models and machine-learning models to aid and accelerate this process.

An electrocatalytic process involves the fundamental steps of reactant adsorption, electron transfer and product desorption. The Sabatier principle, which states that the binding energy between the catalyst and the reactant should be neither too strong or too weak, is usually used in the selection or design of a catalyst[183,184]. However, binding energy is difficult to measure experimentally, especially in complex reaction systems. DFT calculations of binding energy provides a quantitative tool for the application of the Sabatier principle. By building up the atomic structure of the electrode (including the elemental composition, crystalline structure, shape and size) with

appropriate reactant coverage, the adsorption, reaction and desorption free energy can be calculated[185–187]. The calculated binding energies and experimental measurements (such as exchange current densities and limiting potential) of existing catalysts can be utilized to identify the Sabatier principle's ideal range of binding energy, which is then used to guide the design and screening of new catalysts. For example, experimental and computational studies have shown that the binding energy of ˙OH or ˙OOH predicts the catalytic activity for H_2O_2 generation by a two-electron cathodic ORR well[43,111,112]. In addition, DFT calculations have been used for high-throughput screening of HER catalysts[185], and combined DFT calculation and experimental data has been used to identify desired catalysts[188,189]. Similarly, this approach can guide the selection of proper elements to enhance the selectivity for electrochemical water treatment processes by avoiding the unwanted hydrogen evolution side reaction.

Simulating electrochemical processes occurring in water treatment applications can be substantially more challenging, because they involve complex, multistep electrochemical reactions. Nevertheless, research has shown promise in using DFT-based and microkinetic models to assist electrode material screening in recent studies. For example, the relative activity and selectivity among transition-metal catalysts have been analysed for the denitrification process: NO_3^- reduction to form N_2 or NH_3. The adsorption energies of oxygen and nitrogen atoms were identified as appropriate descriptors[190,191]. A joint strategy based on machine learning and computation was used to screen over 50,000 bimetallic alloys and identified 20 materials as promising candidates[192]. These 20 alloys met screening criteria in terms of corrosion resistance, activity, selectivity, cost and ease of synthesis, with the conclusion that Cu-based catalysts (such as Cu–Co and Cu–Ag) were the most promising and worthy of further investigation. These studies are excellent demonstrations of how computational models can be used in the screening and design of electrode materials for water treatment.

DFT calculations of the binding energy at the atomic scale provide the thermodynamic basis for electrocatalytic reactions. What is equally important is the kinetics of these reactions, especially those involving multiple reaction steps. The rate of an electrocatalytic reaction depends strongly on micro- and macroscale mass-transfer processes, which have been less studied. More attention should be paid to mass transfer and other kinetics-related issues in future research.

Design of selective electrode materials

The selective removal or recovery of target solutes from complex background species is an important advantage of electrified water treatment compared with conventional water treatment processes. In addition to designing selective catalysts by tuning their binding energies to the target chemical or intermediate at the atomic level, the selectivity of electrochemical reactions can be improved using a 'trap and zap' approach[22] either by designing the electrode at the nanometre-to-micrometre scale or by optimizing the reactor configuration and operation conditions. This strategy involves selectively 'trapping' the target contaminant on the electrode surface to increase its local or surface concentration, followed by a 'zapping' step that degrades the adsorbed contaminant by direct charge transfer or indirect oxidation and/or reduction by redox mediators (such as ˙OH or ˙H), whose concentrations are highest at the electrode surface. The higher concentrations of both the target contaminant and reactive oxidants and/or reductants are expected to lead to substantially faster reaction kinetics compared with a homogeneous electrochemical process, where the reactive radicals produced on the electrode surface diffuse back to the bulk solution and react non-selectively with both the target contaminant and background species of concentrations usually orders of magnitude higher than the target contaminant.

Several strategies could facilitate the selective 'trapping' of target species. Tuning the electrode pore size and geometry allows for selective transport and adsorption of target contaminant over competing species because of steric hindrance. For example, hierarchical carbon aerogel monoliths with narrow (<1 nm) slit-like pores are well suited to adsorbing the planar, weakly hydrated NO_3^- over Cl^- and SO_4^{2-} (ref. 193). Activated carbon with micropores is used for the selective adsorption of monovalent ions over divalent ions, owing to the differences in their hydrated ion sizes[12,194].

Surface functionalization is also used to improve the electrode selectivity by trapping target contaminants or repelling competing species, utilizing electrostatic (using sulfonate, carboxyl and amine groups)[195–197] and hydrophobic interactions. In addition, ion imprinting − a biomimetic method that creates template-shaped cavities in polymer matrices with high selectivity for target contaminants − has also been used in electrosorption processes to selectively trap species of concern (such as Li^+ (ref. 198) or radionuclides[199]). Composite electrodes with selective coating (such as selective ion exchange[55] or porous[53] films) have also been designed to limit the transport of competing species while allowing the target contaminant to permeate towards the electrode surface or electrogenerated radicals. These 'trapping' mechanisms create high local concentrations of target species and relatively low concentrations of competing contaminants on the electrode surface. Then, the 'zapping' mechanism is designed by atomic engineering of the material properties (crystalline structure, particle shape and so on), guided by computational tools such as DFT to selectively transform the target pollutant to desired products. It is worth noting that adsorption between the electrode and the target contaminants should have the appropriate strength to enable the effective capture of the reactants while avoiding electrode poisoning.

Besides electrodes, the reaction environment can also influence the selectivity of the electrochemical process. For example, ORR is the major competitive reaction in electrochemical denitrification[200]. Therefore, electrode selectivity can be effectively improved by purging with inert gas to expel dissolved O_2. Optimizing the electrolyte to improve the solubility of the target reactant and controlling the pH of the electrolyte (or at least the local pH near the catalyst surface) would influence the reaction activity among different species[201]. In addition, reaction conditions such as temperature, pressure and hydraulic retention time may be adjusted to suppress competing reactions without affecting the selective interaction with target contaminants. For negatively charged contaminants that need to be reduced or for positively charged contaminants that need to be oxidized, electrode polarity switching may enable their electrostatic trapping (adsorption), which is followed by electrochemical reactions when the polarity is switched. However, the optimal reaction environment and operating conditions may be different for different electrocatalysis processes. Therefore, it is important to evaluate specific contaminants in realistic feed waters.

Flow-through electrode for novel process or reactor designs

A high efficiency electrified system requires a compact, modular reactor design and high catalyst utilization efficiency. Conventional electrified reactors consist of a pair of (or multiple) flat plate electrodes and are operated in a flow-by mode. These reactors suffer from slow mass transport, which limits the overall degradation rate, especially when treating water with low pollutant concentrations[202].

Review article

Alternatively, porous flow-through electrodes with high specific surface area, such as electrochemical membranes[203–205] and electrified packed columns[206,207], substantially enhance the overall treatment performance through co-occurring field effects (such as fluid and electric fields) under spatial confinement inside the pores[182,208].

The preparation of flow-through electrodes requires substrates with high porosity and electrical conductivity. Carbonaceous materials, such as CNTs[209–211] and carbon fibres[212], are advantageous, because they can easily form compact and interwoven structures. Metal mesh electrodes consisting of titanium[213,214], iron[215] or copper[216,217] are also promising as conducting substrates. In addition, Magnéli-phase titanium oxides possess desirable electrical properties within a porous monolithic structure and demonstrate good durability during water treatment[218,219]. Flow-through electrodes functionalized with electrocatalysts are generally fabricated using casting or surface modification methods[202]. The porous structure of the electrode can not only increase the number of active sites by providing a higher surface area, but also block foulants from reaching the active sites. In addition, several specific morphologies (such as nanowire and electrically tunable pores) can enable functions such as field-induced reagent concentration[220], microbial electroporation[221] and selective molecular separation[222].

Flow-through configurations enhance contaminant degradation activity and selectivity through various mechanisms, including convection-enhanced mass transport, nanoconfinement effects and enhanced adsorption. Convective transport through the porous electrode decreases the diffusion boundary layer from about 100 μm in the flow-by mode to a length scale comparable to the pore radius of the flow-through electrode, greatly increasing the mass transport rate and maximizing the utilization efficiency of the electrocatalysts[14,223]. Generally, the smaller the pore size and the higher the water flux, the more efficient is the mass transport. When the pore size of the electrode is in the nanometre range, contaminant removal can be further improved by nanoconfinement, which has been reported to enrich the local concentrations of the reactants, reduce the activation energy barrier and modify the pathways and kinetics of reactions[224–226]. Additionally, materials with high specific surface area, such as CNTs, are effective at enhancing the adsorption of the target contaminants owing to decreased mass transfer resistance, increasing the local concentrations of the target contaminants and facilitating subsequent reactions[227,228]. Through these mechanisms, flow-through electrochemical reactors are capable of accelerating reaction rates to several orders of magnitude higher than those obtained in conventional flow-by systems.

The innovative design of synergistic electrified processes expands the functions of the electrode materials beyond those found in traditional electrified processes. For example, a Janus electrochemical membrane, featuring a cathode and an anode on each side, can enable sequential reduction–oxidation reactions in distinct regions of one membrane[229]. A synergistic nanowire-enhanced electroporation and electro-chlorination process achieves complete disinfection under high water flux by aggravating the electroporation-induced damage to microbes with electro-generated active chlorine[230]. Additionally, the application of an alternating potential induces electrophoretic mixing of the concentration polarization layer for fouling control[231]. Notably, the specific energy consumption of these synergistic electrified processes is extremely low (ranging from 10^{-3} to 10^{-2} kWh m^{-3}), owing to their ability to achieve high treatment throughput under low applied voltages (≤2 V).

Electrified flow-through systems can be a viable method of addressing the challenges of conventional electrochemical processes. These systems can achieve high, single-pass contaminant removal at high current efficiency and hence low energy consumption, especially given the synergism among the different processes. The compact and modular construction allows them to be used in large water treatment systems as well as small, point-of-use devices. Future efforts should focus on tailoring macro- to nanostructures of flow-through electrodes (for example, the electrode configuration or the flow channel structure), developing effective techniques to incorporate highly active electrocatalysts without increasing hydraulic resistance.

Outlook

Electrified processes are a promising alternative for a variety of water and wastewater treatment applications and have attracted substantial attention from the scientific community. We foresee continuing research in this area, driven by the increasing need for decarbonization, desalination and water reuse. Energy efficiency, contaminant removal kinetics and the cost and stability of the electrode materials are key metrics that determine the overall performance of an electrified water treatment process. Recent advances in catalyst discovery, electrode fabrication and process optimization have greatly improved these metrics. Notably, novel catalysts (such as single atoms, bi- and tri-metals and oxides) and electrode structures (such as porous plate or film, fluidized suspension, packed bed and electrode stack) designed for specific processes and novel operation modes (such as constant voltage and polarity reversal) have focused on improving target contaminant mass transfer and enhancing transformation kinetics following preferred reaction pathways. These existing studies provide valuable data for future materials screening and design, especially for artificial intelligence (AI)-based approaches such as machine learning, which requires large datasets. However, despite the large number of studies reporting the performance of electrode materials for water treatment, these often vary substantially in reactor design, water chemistry, operation conditions and target contaminants, and the information reported is often highly fragmented. There is a strong need for a database or repository where the performance data of electrode materials, together with other relevant information, can be deposited. A shared database with research-grade data could greatly facilitate future computational and experimental research on electrode material screening and design.

Another important research need is the integration of electrified treatment with other processes to generate synergy that addresses the limitations of each process or create additional benefits such as production or recovery of valuable chemicals and energy storage. For example, integration of the electrochemical process into membrane filtration (where the porous electrode also serves as a filtration membrane) improves the mass transfer of contaminants to the electrodes by convective transport while decreasing membrane fouling by degrading organic and biological foulants[232]. Bioelectrochemical systems couple the electrochemical process with biological degradation, where electrochemical reactions improve the biodegradability of contaminants while microorganisms break down electrochemical reaction by-products, leading to better mineralization[233]. In addition, integrated systems can be designed to take advantage of hydrogen produced through the HER on the cathode[234], or the acid and basic conditions near the surface of the electrodes or bipolar membranes. Other processes and techniques, such as photocatalysis, flocculation, flotation, disinfection, steam generation, ultrasonication and microwave treatment can also be integrated with electrochemical processes directly or indirectly. In these integrated systems, design of the electrode material must not only consider the target electrochemical

Review article

reactions, but also the characteristics desired for the other processes, such as the pore structure and size distribution for membrane filtration, surface characteristics suitable for biofilm formation and growth, stability as a function of pH and the flexibility to accommodate novel reactor configurations. Such multifunctional systems will embody future water treatment.

A well-recognized challenge in water treatment is the complexity and variability of source-water quality. Therefore, much research has been devoted towards improving electrode selectivity and activity towards target contaminants relative to competing background species. Less has been done to achieve selectivity among reaction pathways and/or products. We recommend that future research also consider selectivity towards desired products, that is, those that are benign or of high value, in order to minimize the total toxicity and other potential environmental impacts of effluent while finding ways to offset treatment cost. This would require advanced techniques for characterizing interfacial processes in situ, another important future research need. We emphasize that selectivity for both target contaminants and desired reaction pathways and/or products is a strong function not only of electrode material properties, but also of electrode and reactor configurations as well as operating conditions. Therefore, understanding the processes involved from atomic to device scale is necessary. Furthermore, research on electrode activity and selectivity, either experimental or computational, needs to be performed in realistic solution chemistry and under realistic flow conditions in order to represent the relevant mass transport and reaction processes. This requirement is especially important when comparing different electrode materials for a specific application.

In summary, electrified water treatment will have a central role in future-generation water treatment systems. Research on electrode materials is critical to achieving high performance while bringing down the cost. Future research should move beyond the simple evaluation of the target contaminant removal and should focus on developing high-performing materials that not only have high selectivity and activity towards the target contaminants in the wide range of solution chemistry encountered in natural and wastewater, but also produce desirable products that are benign or of high value. It is also increasingly important for electrodes to be multi-functional, allowing the synergistic incorporation of other treatment processes with the electrified process. Computational chemistry and AI-based material discovery and screening will be essential tools in future research.

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Author contributions

K.Z., S.G.-S., G.A.C.-C., F.-Y.C., X.T., X.W., X.H. and Q.L. researched data for the article. K.Z., S.G.-S., H.W., P.J.J.A., J.L., M.E. and Q.L. contributed substantially to discussion of the content. K.Z., S.G.-S., G.A.C.-C., F.-Y.C., X.T., X.W., X.H. and Q.L. wrote the article. K.Z., S.G.-S., H.W., P.J.J.A., J.L., M.E. and Q.L. reviewed and/or edited the manuscript before submission.

Competing interests

The authors declare no competing interests.