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Molecularly Selective Polymer Interfaces for Electrochemical Separations

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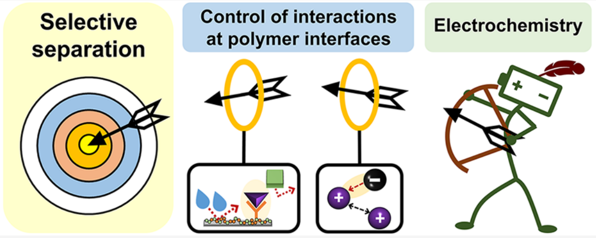

ABSTRACT: The molecular design of polymer interfaces has been key for advancing electrochemical separation processes. Precise control of molecular interactions at electrochemical interfaces has enabled the removal or recovery of charged species with enhanced selectivity, capacity, and stability. In this Perspective, we provide an overview of recent developments in polymer interfaces applied to liquid-phase electrochemical separations, with a focus on their role as electrosorbents as well as membranes in electrodialysis systems. In particular, we delve into both the single-site and macromolecular design of redox polymers and their use in heterogeneous electrochemical separation platforms. We highlight the significance of incorporating both redox-active and non-redox-active moieties to tune binding toward ever more challenging separations, including structurally similar species and even isomers. Furthermore, we discuss recent advances in the development of selective ion-exchange membranes for electrodialysis and the critical need to control the physicochemical properties of the polymer. Finally, we share perspectives on the challenges and opportunities in electrochemical separations, ranging from the need for a comprehensive understanding of binding mechanisms to the continued innovation of electrochemical architectures for polymer electrodes.

1. INTRODUCTION

Electrochemical separations have garnered intense interest due to their modularity, sustainability, and applicability in critical areas of societal importance such as water purification, environmental remediation, and the recovery of value-added molecules for manufacturing.[1−3] There is a growing emphasis on the development of selective separation methods to decrease energy consumption, carbon footprint, and costs.[4−6] A notable advancement in liquid-phase electrochemical separations has been to extend the binding mechanisms beyond solely electrostatic and double-layer effects in capacitive carbon electrodes and leverage specific interfacial interactions such as hydrophobicity, conformational effects, size exclusion, and noncovalent binding at polymer-functionalized interfaces (Figure 1). A transition toward these functionalized electrodes has enabled the selective separation of minority species from majority competing species, shifting the focus from the adsorption of the charged species from the solvent stream (e.g., as in desalination) to discriminating a desired target from multicomponent mixtures. Modulating molecular-level interactions has been pivotal to controlling selectivity in electrochemical separations, with macromolecular design being key to achieving interfacial specificity in electrosorption as well as membrane permselectivity in electrodialysis.[4]

Polymer interfaces have been core components in the design of stimuli-responsive systems. In the past, conducting polymers have been extensively studied as electroactive films for anion doping.[7−10] Since then, redox-responsive polymers have been applied to numerous applications including electrochemical sensing,[11] catalysis,[12−14] and energy storage.[15,16] However, despite their intrinsic capabilities for ion-selective interactions, only recently have redox polymers been systematically investigated for the separation of diverse charged molecules, particularly anionic species.

The systematic design and investigation of redox-active polymers have enabled unprecedented anion selectivity in electrosorption platforms, going beyond the capabilities of conventional intercalating and reactive materials. Prior work on crystalline electroactive materials (e.g., $LiMnO_2$ and Prussian blue analogues) as well as reactive electrode materials (e.g., Ag/AgCl and Bi/BiOCl) has been predominantly centered around cation-selective separations,[17−20] and in the few instances when anions were targeted, they were mostly limited to chloride.[21,22] Switchable redox-active polymers have dramatically expanded the target species scope, enabling the selective removal of toxic anionic species such as per- and polyfluoroalkyl substances (PFAS),[23−25] the recovery of

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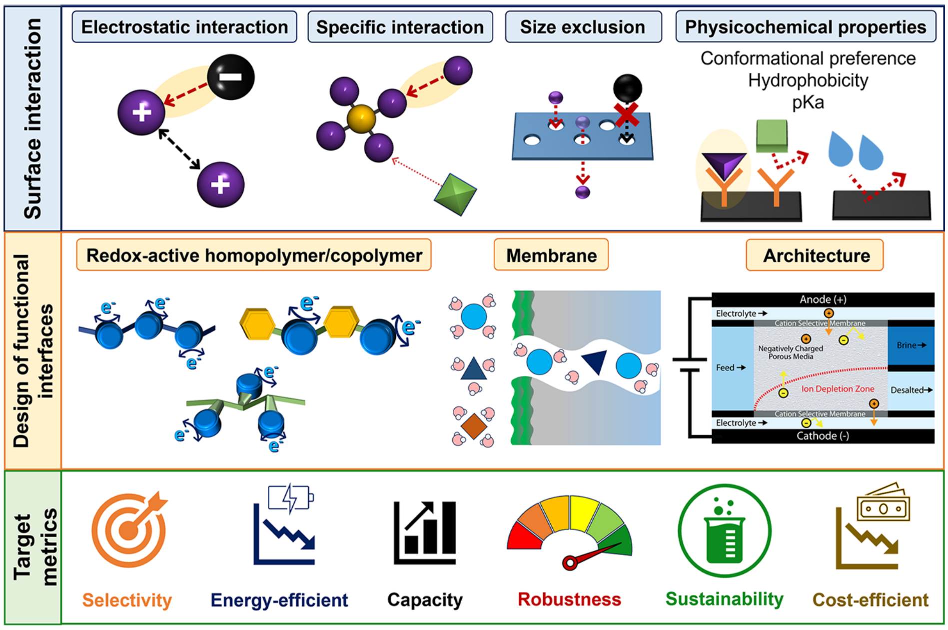

Figure 1. Overview of specific interactions associated with polymer interfaces, pathways for polymer design and electrochemical architecture engineering, and target metrics in electrochemical separations.

valuable anionic species such as gold from electronic waste,[26] and also the recycling of homogeneous catalysts from chemical processes.[27] Upon the oxidation of redox-active polymers, anions can be selectively captured via specific intermolecular interactions and subsequently released upon the reduction of the redox moieties. The overall selectivity of the redox-active polymers relies on a combination of electrostatic interactions and conformational and solvation effects.[1,3,23,28,29]

Polymer design is also crucial to guaranteeing the selectivity and robustness of electrodialysis membranes. Ion-exchange membranes (IEMs) play a key role in directing ion migration for desalination[30,31] and resource recovery.[32,33] Cation-exchange membranes incorporate negatively charged functional groups such as sulfonate groups, while anion-exchange membranes contain positively charged groups such as quaternary ammonium groups, allowing them to selectively transport cations or anions under electric fields. More recently, there has been growing interest in the functionalization of IEMs with polymers to address membrane fouling,[34] enhance membrane permselectivity,[35,36] and facilitate ion transport.[37]

In this Perspective, we present a comprehensive overview of recent advances in polymer interfaces for selective electrochemical separations. We discuss chemical design pathways for polymer interfaces and their application in redox-mediated electrosorption and membrane-integrated electrochemical processes (Figure 1). Furthermore, we present the current challenges in the field and future research directions to address these limitations through a comprehensive understanding of molecular-level interactions, material synthesis, and a combination of functionalized interfaces with electrokinetic effects.

2. ACHIEVING SELECTIVITY IN REDOX-MEDIATED ELECTROSORPTION: TRANSITIONING FROM HOMOPOLYMER TO COPOLYMER DESIGN

The advancement of novel materials frequently involves the integration of a broad spectrum of intermolecular interactions, such as electrostatic interactions, charge-transfer interactions, and hydrogen bonding. Utilizing redox-active polymers as immobilized electrosorbents offers numerous advantages as it allows for the incorporation of substantial quantities of adsorbents within a heterogeneous platform and provides versatile selectivity through tailored monomer design. Redox-active polymers are often coated onto electrode substrates with conductive carbon materials, such as carbon black and carbon nanotubes, to improve both electrical conductivity and electron-transfer capabilities.[38] This composite allows an increase in the available surface area for uniform deposition onto substrates such as carbon paper and stainless steel mesh, leading to an enhanced overall uptake of target species and improved charge efficiency.[38] Redox-active polymers possess sites that can be switched on/off by an applied potential or current, enabling reversible binding or the release of target species. The selectivity of redox polymers can be not only controlled by the electrochemical properties of redox-active centers but also fine-tuned further through the incorporation of non-redox-active pendant groups into the redox-active center[23,39−42] and non-redox-active moieties into copolymer design.[25,43−45] Consequently, the careful selection of redox-active centers, non-redox-active functional groups, and appropriate polymer design has been a long-standing topic of interest in achieving highly selective and efficient separation processes.

2.1. Design of Redox-Responsive Homopolymers.

Redox-responsive homopolymers have gained attention in electrochemical separation owing to their simple yet robust polymer structures consisting of repetitive single redox-responsive monomer units. Free radical polymerization and electropolymerization have been widely used for the synthesis of redox-active polymers for electrochemical separation due to their facile synthesis.[39,46,47] In addition, the reversible addition−fragmentation chain transfer (RAFT) method is frequently employed as a polymerization technique to precisely control the molecular weight distribution of polymers.[23,48,49] Redox-active homopolymers can be classified into two categories based on the arrangement of the redox-active units within their chemical structures, as depicted in Figure 2:

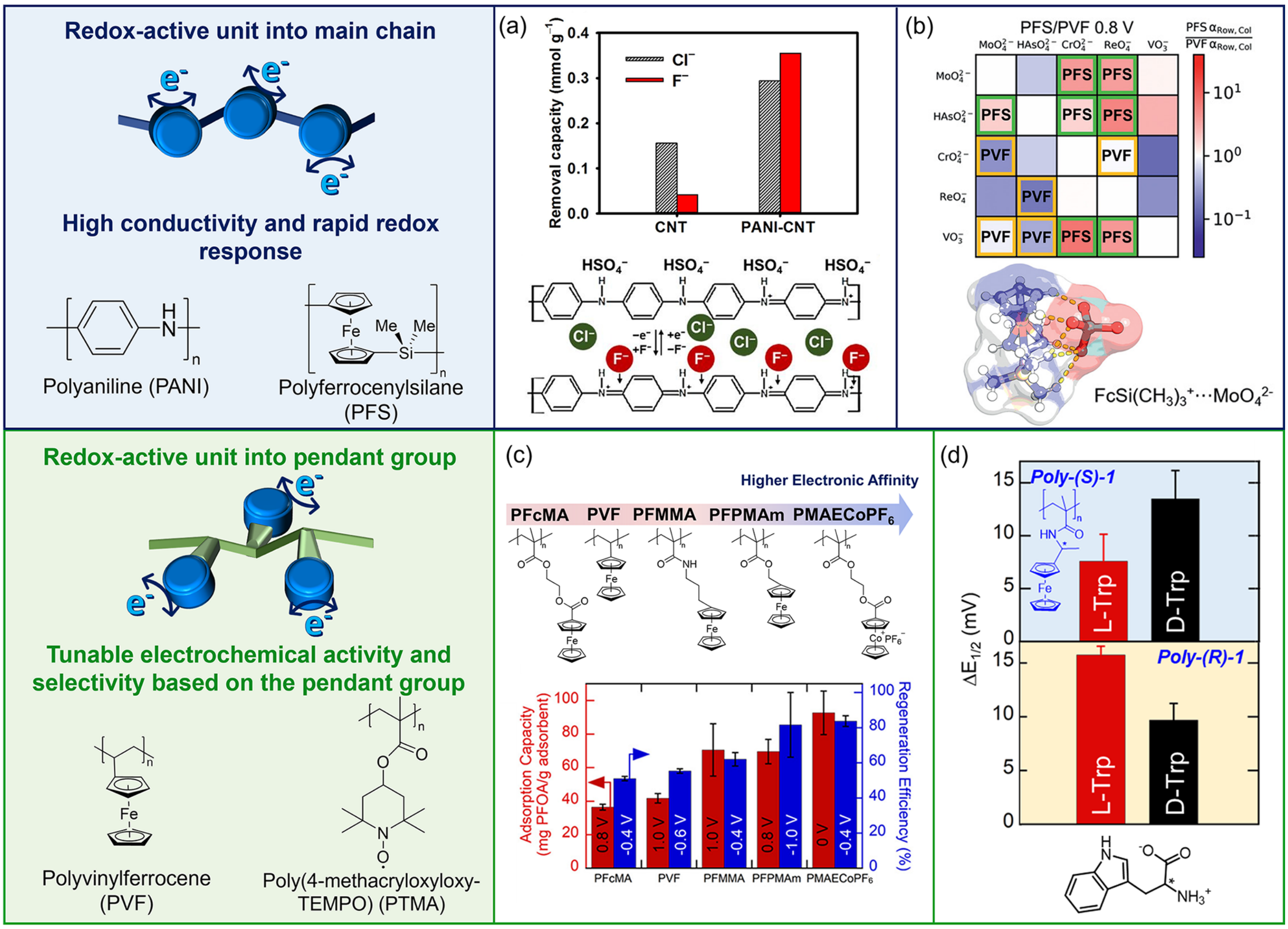

Figure 2. Classification of redox-responsive homopolymers based on the incorporation of redox-active units: (a) polyaniline (PANI) and (b) polyferrocenylsilane (PFS), featuring redox-active units in the main chain, (c) ferrocene and cobaltocene derivatives, and (d) chiral ferrocene polymers, featuring redox-active units in pendant groups. Panels a−d are reprinted with permission from refs 51 (copyright 2021 Elsevier) for panel a, 55 (copyright 2021 Wiley) for panel b, 23 (copyright 2023 American Chemical Society) for panel c, and 39 (copyright 2023 Wiley) for panel d, respectively.

(i) incorporation of the redox-active center into the polymer backbone[47,50−55] and (ii) attachment of the redox-active unit as a pendant group.[23,24,26,27,38,39,56−58]

Polyaniline (PANI),[47,51] polypyrrole,[50,58] poly(3-hexylthiophene-2,5-diyl),[52] poly(*m*-phenylenediamine),[53] and polyferrocenyl-silane (PFS)[55] involve the redox-active units embedded in the main chain. This direct attachment facilitates efficient charge transfer and conductivity, resulting in robust kinetics for electrosorption and release in a wide range of selective separations such as the selective recovery/removal of ammonium,[47] heavy metals,[50,53,54] and mercury.[52] PANI, in particular, has been successfully employed in various separation applications such as fluoride removal (Figure 2a)[51] and nitrate capture.[47] The robust charge−charge interactions with highly electronegative species facilitate the selective capture of these anions through hydrogen bonding. Consequently, fluoride demonstrates more favorable interactions with PANI than chloride, resulting in a 4.7-fold increase in selectivity with 153% enhanced F^- uptake compared with the CNT control electrode. Furthermore, Kwiyong et al. achieved the selective capture of nitrate over chloride simultaneously with ammonium conversion by integrating PANI with Co_3O_4 as a bifunctional polymer electrode.[47] The selectivity for nitrate was achieved through a combination of electrostatic interactions and hydrogen bonding, resulting in a selectivity factor of up to 3.45 when PANI is in the form of a pernigraniline salt (PS). The selective capture and up-concentration of nitrate enabled more efficient ammonium production during the regeneration step, leading to a 24-fold increase in the ammonium production rate compared to that of direct electrocatalysis in a dilute nitrate solution.[47]

In the case of PFS, the selectivity among oxyanions is further influenced by the nearby interaction of ferrocene-ferrocene (Fc-Fc).[55] As the neighboring ferrocene moiety is oxidized, the reduced ferrocene unit experiences an electron-withdrawing effect, resulting in positive shifts in the $E_{1/2}$ potential. This semiconductive nature of PFS, stemming from a two-step oxidation process, alters ion-selectivity trends and enhances selectivity in comparison to those of polyvinylferrocene (PVF) (Figure 2b). For example, PFS demonstrated a 7.5-fold increase in selectivity for VO_3^- over CrO_4^{2-} compared to that of PVF, which contains a redox-active unit in the pendant group.[55] The near-neighbor effect in PFS leads to the delocalization of positive charge on the silicon atom, and thus, the methyl groups of the silane provide additional binding sites for oxyanions (Figure 2b). As a result of this

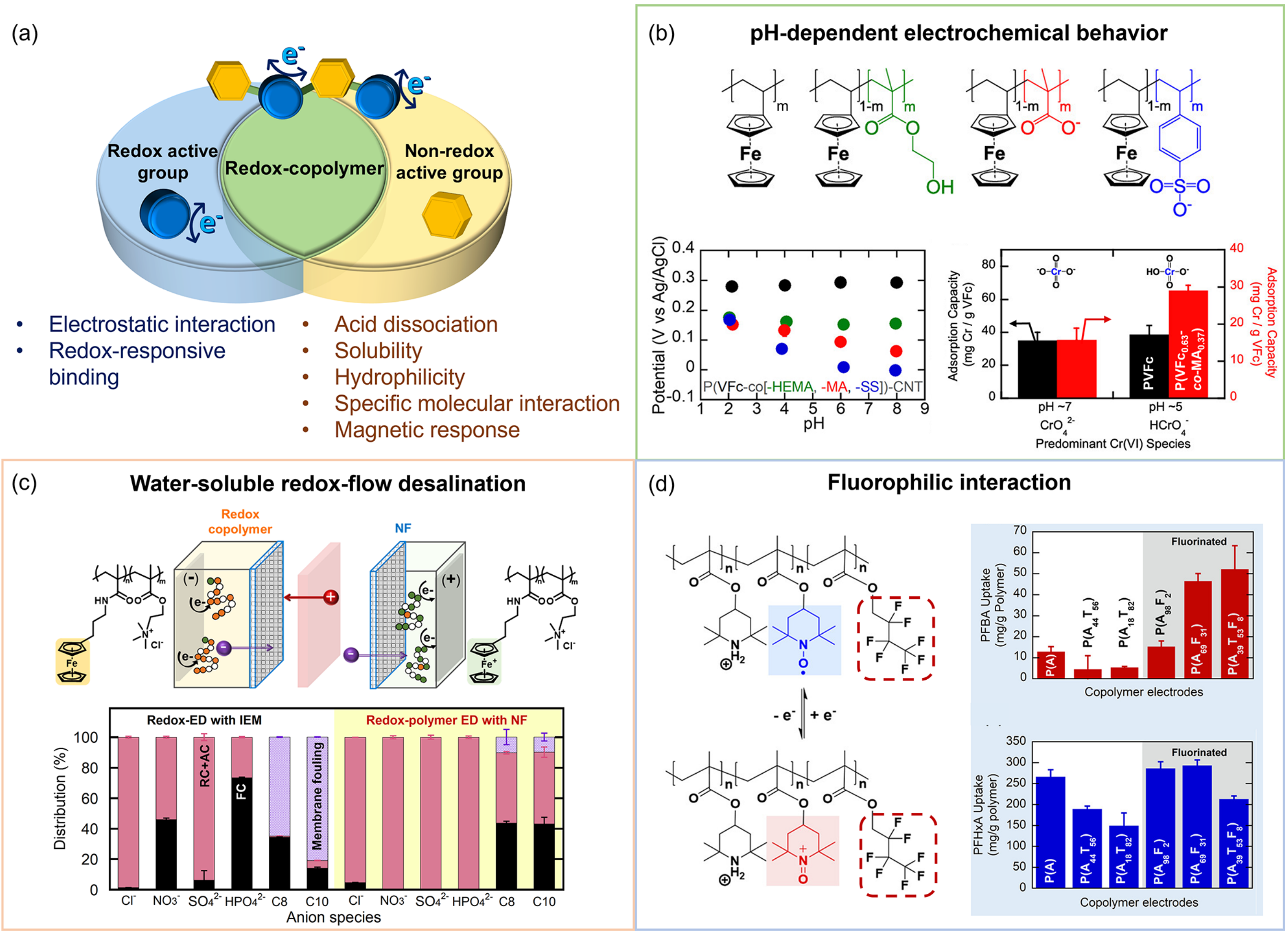

Figure 3. (a) Design of redox copolymers and their properties, featuring the copolymerization of redox moieties with various non-redox-active moieties for (b) pH-dependent electrochemical behavior, (c) water-soluble redox copolymer, and (d) fluorophilic interactions. Panels b, c, and d are reprinted with permission from refs 43 (copyright 2023 American Chemical Society) for panel b, 45 (copyright 2023 American Chemical Society) for panel c, and 24 (Copyright 2023 American Chemical Society) for panel d, respectively.

additional interaction, the binding affinity of PFS was altered compared to the selectivity of PVF, exhibiting a preference for MoO_4^{2-} over CrO_4^{2-} and $HAsO_4^{2-}$ over ReO_4^{-}.[55]

While incorporating the redox-active unit into the main chain of metallopolymers allows for robust electrochemical responsive electrosorption and release, it can present challenges in modulating the strength of electrostatic interactions and maintaining polymer stability.[59−61] Besides, the modification of main-chain polymers can often increases the complexity of the synthesis. On the other hand, when a redox-active unit such as ferrocene,[23,26,27,38,56−58] cobaltocene,[23,58] or TEMPO[24,38] is attached as a pendant group of polymers, the electrochemical activity or selectivity of redox-active metallopolymers can be effectively modulated based on the electrochemical and physicochemical properties of the non-redox-active pendant group while enhancing the polymer stability.[41,62] This approach also allows for more facile and modular synthesis routes for the creation of the polymer itself.

In particular, the electrochemical properties of the redox-active centers vary depending on the electron delocalization capability or even the regioselectivity of the non-redox-active group. As seen in Figure 2c, the incorporation of a stronger electron-donating group, propyl methacrylamide, into the ferrocene-based polymer structure, poly(3-ferrocenyl-propyl methacrylamide) (PFPMAm), led to an increase in the capacity and the release of perfluorooctanoic acid (PFOA) compared to polymers such as PVF and poly(2-(methacryloyloxy)ethyl ferrocene carboxylate) (PFcMA), which involves an electron-withdrawing group.[23] Interestingly, among metallopolymers with the same non-redox-active group, cobalt-based metallopolymer poly(2-(methacrylolyoxy)ethyl cobaltoceniumcarboxylate hexafluorophosphate) ($PMAECoPF_6$) exhibited higher capacity and reversibility for PFAS removal compared to iron-based metallopolymers (PFcMA). This highlights the significance of both the electron-donating effect of the non-redox-active group and the electrochemical reactivity of the redox-active center.

To expand the capabilities of redox-metallopolymers even further, imparting a chiral center to the ferrocene moiety enables electrochemically controlled enantioselective interactions toward amino acids (Figure 2d).[39] A chiral metallopolymer (poly-1) was synthesized by replacing the amine group in Ugi's amine (*N*,*N*-dimethyl-1-ferrocenylethylamine) with an amide group, positioning the chiral center adjacent to the cyclopentadienyl rings of ferrocene. The chirality of the metallopolymer determined its selective affinity for specific enantiomers, resulting in an opposite favorability for each enantiomer. The steric hindrance originating from the chiral center played a key role in interacting preferentially with the target molecules containing bulky aromatic groups, such as tryptophan and naproxen.[39]

Overall, the regulation of molecularly selective polymer interfaces can be accomplished by modulating the electrochemical and physicochemical properties using various homopolymer configurations. Hence, it is crucial to have a comprehensive understanding of the electrochemical and physicochemical properties of redox-active polymers as well as a careful examination of the chemical properties of both the target and any undesired species that might coexist in the solution.

2.2. Toward Copolymer Design in Electrochemical Separation Technologies. Designing redox copolymers with non-redox-active functional groups offers a promising strategy to increase the degree of control over the intermolecular interactions by having distinct monomer chemistries within a single polymer chain. Given the currently limited selection of stable and efficient redox-active groups, the incorporation of non-redox-active groups within copolymers facilitates the development of unique physicochemical properties, without direct participation in electron-transfer reactions. Consequently, the design of the redox-active copolymer can exhibit exceptional selectivity based on the combination of electrostatic interactions of redox-active groups with the hydrophilicity,[43,63,64] solubilities,[45] electrostatic repulsions,[43,44] and specific molecular interactions[24,65] of the non-redox-active pendant groups (Figure 3a). Thus, the transition from a homopolymer to a copolymer design enables a broader range of material choices, ultimately expanding the scope of potential applications of electrochemical separation technologies. Most of the copolymers utilized in selective separation have been synthesized using the free radical copolymerization method, achieving a statistical distribution of both monomers within the copolymer structure.

Leveraging the hydrophilicity and pH-dependent behavior of the non-redox-active groups has been widely applied in copolymer synthesis, aiming to enhance both selectivity and reversibility.[43,44] For instance, the copolymerization of FPMAm with methacrylic acid (MAA) allows cation-selective separations, particularly the rare earth elements (REEs), including yttrium(III), neodymium (Nd), and europium (Eu).[44] The MAA moiety interacts with the REEs through ion exchange, while the redox-active ferrocene unit on the FPMAm releases the bound REEs through electrostatic repulsion driven by an electrochemical potential. The combination of ion-exchange adsorption with electrochemical release extends the scope of applications for redox-active polymers to cation-selective separations. Furthermore, the copolymerization of vinyl ferrocene with acid-dissociable non-redox-active moieties, such as 2-hydroxyethyl methacrylate (HEMA), methacrylate (MA), and 4-styrenesulfonate (SS), has been shown to exhibit pH-dependent electrosorption of transition-metal oxyanions (Figure 3b).[43] Depending on the acidity strength in the non-redox-active groups (SS > MA > HEMA), the electrochemical properties can be tuned by the solution pH. For instance, P(VF-*co*-MA) and P(VF-*co*-SS) exhibited distinct redox activity and $E_{1/2}$ values at different solution pH. On the other hand, the electrochemical properties of P(VF-*co*-HEMA), which contains the least acidic non-redox-active group, remained unaffected by changes in the solution pH. Under acidic conditions, P(VF-*co*-MA) showed enhanced uptake of transition-metal oxyanions, with remarkable selectivity for hydrogen chromate (CrO_4^-) over dichromate due to electrostatic repulsions from the partial dissociation of non-redox-active moieties (Figure 3b). In addition, the hydrophilic non-redox-active moieties synergistically enhanced the overall hydrophilicity of redox copolymers to facilitate the oxidation of ferrocene at lower potentials than PVF by promoting favorable charge-transfer interactions.[43]

The advancement of a water-soluble redox copolymer has served as a significant milestone in addressing major limitations associated with the use of ion-exchange membranes (IEMs) in electrodialysis systems, including high costs and membrane fouling (Figure 3c). A water-soluble moiety, [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (METAC), was copolymerized with the ferrocene moiety as P(FPMAm-*co*-METAC) to create a polymer-based redox mediator that can drive the removal of charged species and produce clean water.[45] The redox reaction by the soluble copolymer replaces water electrolysis and lowers the operating voltages for desalination. Through the substitution of IEMs with more affordable and robust nanofiltration membranes (NFs), the redox-polymer electrodialysis system demonstrated continuous removal of both inorganic and organic components from wastewater down to a potable water range, while effectively preventing the fouling of organic species on the membranes (Figure 3c).[45]

Redox-copolymer design has also evolved as a promising approach to the effective removal of emerging contaminants, perfluoroalkyl substances, and polyfluoroalkyl substances (PFAS), known as forever chemicals. PFAS removal is challenging due to their chemical persistence and dilute concentrations found in water, typically within the parts per billion range.[23−25,66,67] A redox copolymer composed of 4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TMA) and 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine (TMPMA) has exhibited exceptional performance in the removal of long-chain PFAS by tailoring the hydrophobicity, N−H interactions, and electrostatic interactions. For instance, P(TMA_{51}-*co*-$TMPMA_{49}$) has demonstrated a remarkable uptake capacity (>1,000 mg/g) of perfluorooctanoic acid (PFOA) and electrochemical reversibility over 90%.[65] On top of the electrostatic interactions of TMA and amine interactions of TMPMA, the fluorophilic interaction of 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFBMA) was utilized as a specific molecular interaction to target short-chain PFAS, with carbon chain lengths ranging from C_4 to C_7 (Figure 3d).[24] Fluorocarbon groups on the PFAS facilitate dipole−dipole or point−dipole interactions with a fluorinated nonredox moiety, HFBMA, through intermolecular dispersion interactions, commonly referred to as fluorophilic interactions. The incorporation of fluorinated redox-active amine functionalities into various copolymer combinations elucidated the significance of fluorinated interactions in the removal of less hydrophobic short-chain PFAS ($C_{n\leq5}$) was elucidated. In the presence of fluorinated functionalities within the copolymers, P(AF) and P(ATF), the uptake of perfluorobutanoic acid (PFBA, C_4) was increased 10-fold (Figure 3d).[24] Furthermore, monomer MD simulations underlined the importance of neighboring functional groups and their distribution for achieving a synergistic effect involving electrostatics, amine interactions, and fluorophilic interactions while also preventing copolymer chain agglomeration.[24]

Thus, in both redox-active homopolymer and copolymer structures, a comprehensive understanding of various polymer

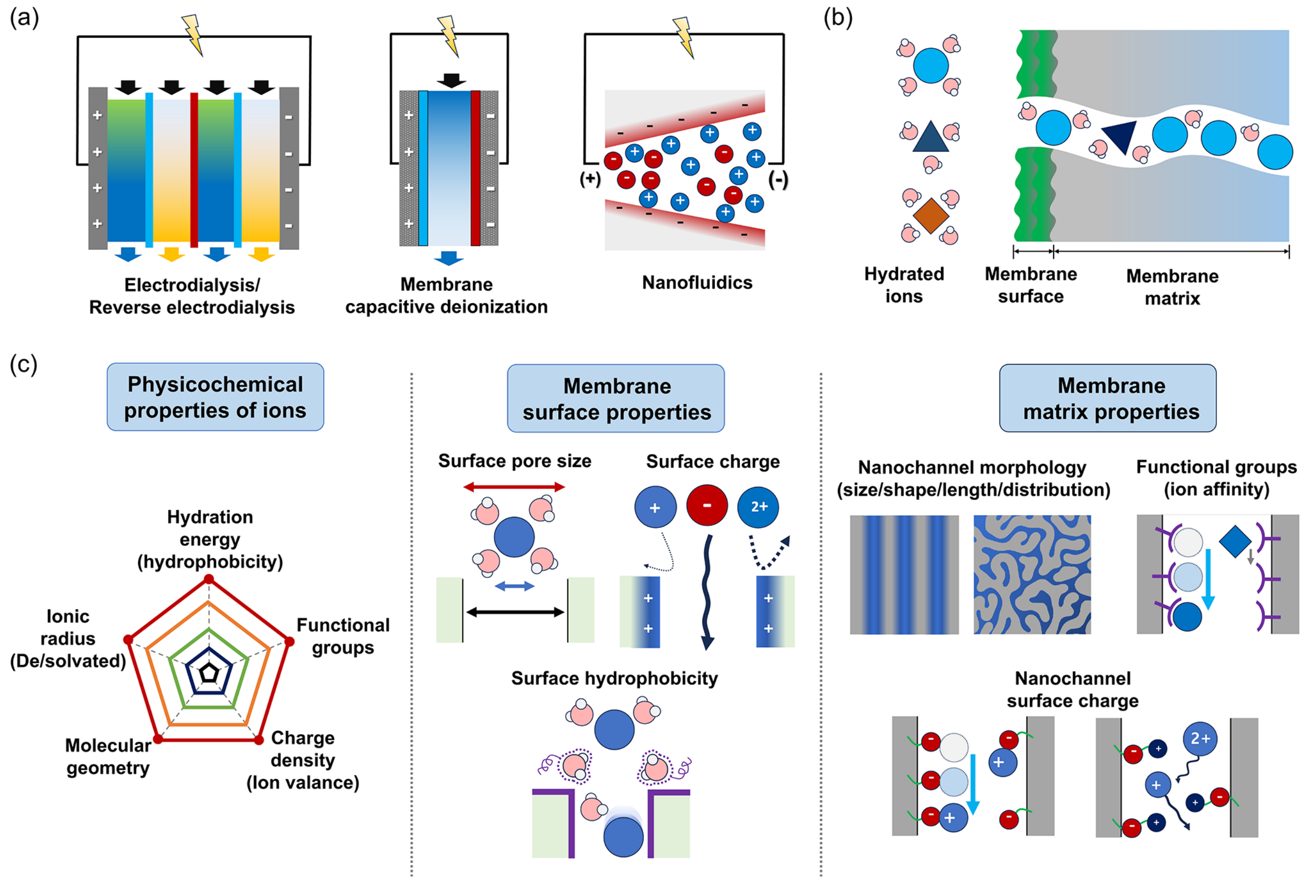

Figure 4. Overview of membrane-based electrochemical separation and selectivity mechanisms: (a) examples of electrochemical separation systems, (b) solution−membrane interface showing the transport of specific ions, and (c) physicochemical properties of ions and membrane properties tuned to achieve ion permselectivity.

characteristics, including morphology, conformation, hydrophobicity, solvent interaction, and thermal properties, is of utmost importance in improving the molecular selectivity, electrochemical stability, reversibility, and overall performance of the materials. Moving ahead, we firmly believe that investigating complex molecular binding mechanisms, including near-neighbor and copolymer-level interactions, is crucial for advancing the performance of redox electrodes for electrosorption. Gaining a comprehensive understanding of the physicochemical and electrochemical properties of both target and competing species as well as solvent interactions and binding strength in diverse solvents is vital to effectively modulating the binding affinity between redox polymers and target species. Moreover, future research directions may entail the development of more efficient and environmentally friendly synthesis methods to enable the large-scale production of polymers for industrial applications.

3. MEMBRANE-DRIVEN ELECTROCHEMICAL SEPARATION

Polymeric membranes are critical components of electrochemical ion-separation processes, including electrodialysis (ED), membrane capacitive deionization (MCDI), and nanofluidics (Figure 4a). Membrane-based electrochemical separation systems leverage electrodiffusion through ion-selective membranes under applied electric fields to remove salts. The hydrated ions migrate toward the membrane surface and are transported through the membrane matrix, as shown in Figure 4b. Thus, the characteristics of the outermost surface and membrane interior channel play a key role in imparting selectivity between target ions and competing ions, with enhanced ion mobility for target species. The functionalization of membranes is often achieved by altering the physicochemical properties of the ions, which include the ionic radius (e.g., hydrated radius and Stokes radius), hydrophobicity, molecular geometry, ion valency, and functional groups.[68]

3.1. Selectivity Mechanisms in IEM. The selectivity of IEM is tailored to reject specific ions relying on the following effects: (i) pore-size sieving effect, (ii) electrostatic repulsion, (iii) hydrophobicity of the membrane surface, and (iv) membrane morphology (Figure 4c). The pore-size sieving effect is determined by the hydrated size of ions relative to the effective pore size of the membrane, which is typically in the micropore range (diameter <2 nm according to the IUPAC definition).[69] Ions are typically surrounded by water molecules in an aqueous environment, and the degree of hydration varies depending on the physicochemical properties of each ion. In general, ions with a hydrated radius larger than the surface pore size have difficulty entering the membrane matrix unless they are partially dehydrated by interaction with the surface. This size-based selectivity is widely utilized to separate inorganic ions from bulk-charged species.[70] The selectivity based on size also facilitates the control of ion migration in the presence of bulk-charged species that are unable to cross over the IEMs.[71,72] Nonetheless, the membrane pore size has a limited effect on distinguishing between inorganic ions with

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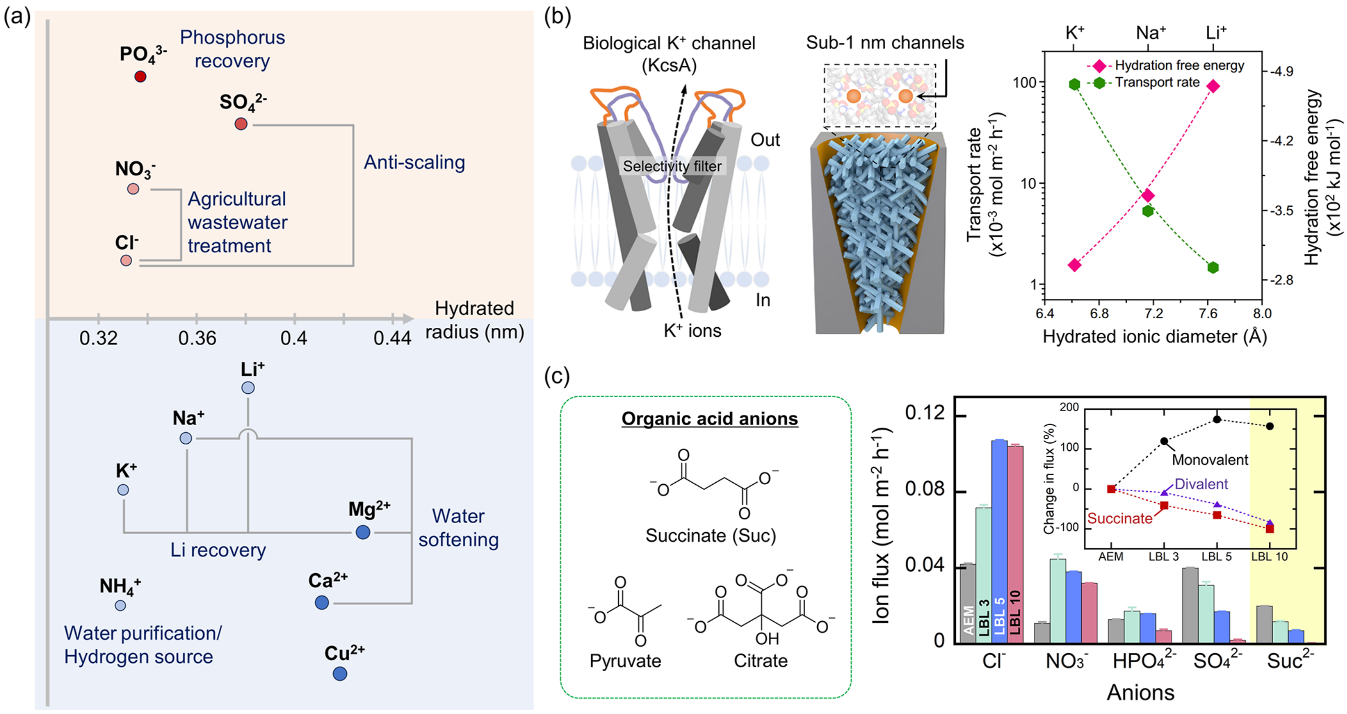

Figure 5. Challenges in electrochemical ion separation and representative membrane functionalization for the enhancement of the selectivity: (a) schematic of challenging ion separation drawn with hydrated ionic radius. (b) K^+ channel-mimetic monovalent cation separation membrane and (c) selective organic ion separation using the redox-electrodialysis system. Panels b and c are reprinted with permission from refs 90 (copyright 2022 Nature) for panel b and 5 (copyright 2023 Wiley) for panel c, respectively.

comparable hydrated sizes and often leads to fouling problems in the presence of charged organic species.

The selectivity of IEMs is significantly influenced by the surface charge of the membrane as it either promotes or impedes ion migration at the solution−membrane interface. Since the surface of IEMs is functionalized with either positive (anion-exchange membranes) or negative functional groups (cation-exchange membranes), an attractive force facilitates the migration of oppositely charged species through the membranes. On the other hand, species with the same charges as the membrane are subjected to strong repulsive forces, leading to their rejection. In addition, within the same charged species, a stronger repulsive force is exerted on multivalent ions than on monovalent ions, reducing the permeability of multivalent species and thereby increasing the monovalent ion permselectivity.[73] Nevertheless, an excessively high charge density would concurrently diminish the overall permeability.[74] Thus, a diverse range of charged polymers have been applied to IEM or nanofiltration supports to enhance the permselectivity while maintaining the overall permeability.

The hydrophobic nature of the IEM membrane is also crucial in governing the selective permeation of charged species. As ions cross the membranes, they experience a degree of partial dehydration primarily influenced by the Gibbs hydration energy (ΔG_{hyd}) of the ions and the hydrophobic nature of the membrane surface. It has been shown that the hydrophobic domains hinder the movement of strongly hydrated ions (higher ΔG_{hyd}) while less-hydrated ions can retain their permeability.[75] Moreover, the hydrophobicity of the IEM is closely related to the membrane swelling and permeability. Often, an increase in the membrane hydrophilicity enhances the overall membrane permeability, yet this approach can result in membrane swelling and a subsequent decrease in selectivity. In this regard, several membrane modifications have centered on tailoring membrane hydrophobicity while mitigating membrane swelling.

Beyond the surface properties of IEMs, the physicochemical properties of the membrane matrix play a vital role in fine-tuning the ion mobility and permselectivity during transport within the hydrophilic ion pathways.[76] The ion transport through dense (nonporous) membranes will be critically dominated by such ion−matrix interactions. Homogeneous IEMs are typically composed of a tortuous hydrophilic nanochannel and hydrophobic matrix formed by phase separation. The chemical structure of the polymer matrix (e.g., backbone structure, side chain groups, and topology) determines the morphological characteristics, including the free-volume content, tortuosity, and pore size distribution.[77] To achieve high ion selectivity, it is necessary to construct well-defined subnanometer ion channels with a rigid framework against swelling by water,[78] which was recently showcased by polymers of intrinsic microporosity and covalent organic framework membranes.[79] Additionally, the charged ion exchange groups of the membrane matrix can facilitate or inhibit ion transport within the nanochannels based on the electrostatic interaction. The permselectivity between cation and anion can be enhanced by anchoring the charged groups to reject ions of the same signs (Donnan exclusion). In general, increasing the ion exchange capacity (IEC) or charge density of the membrane (charges per nanometer) enhances ion conductivity. However, there exists a compromise between ion selectivity and ion permeability due to swelling of the polymer framework when it is highly hydrated by the ion exchange groups. Hence, there is a need to optimize the charge density within the matrix and the hydrophilic nature of membranes to improve both the membrane durability and ion permeability.

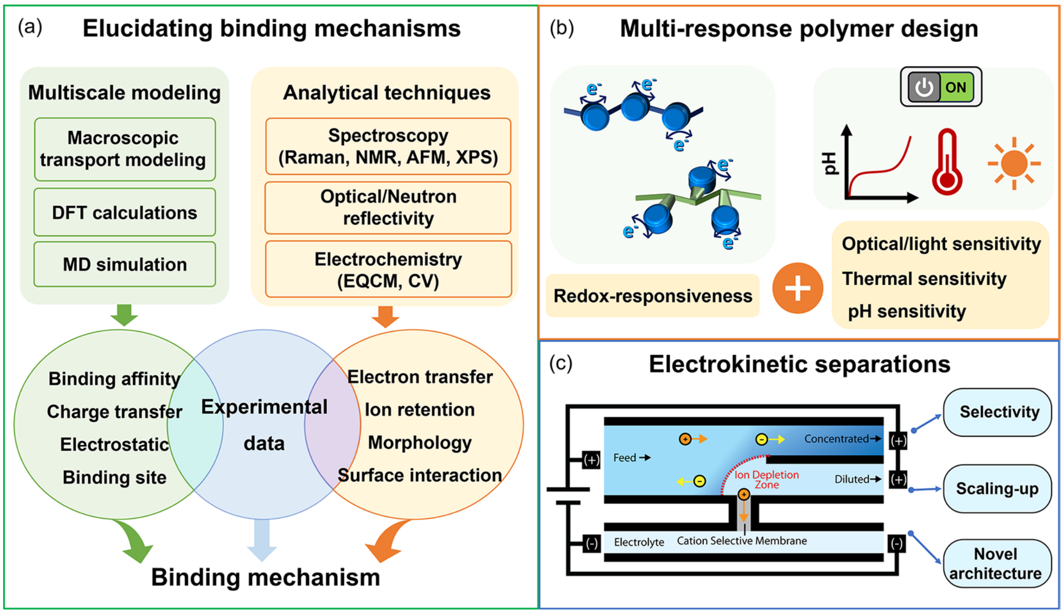

Figure 6. (a) Combination of multiscale modeling and sophisticated analytical techniques for elucidating binding mechanisms. (b) Multiresponse polymer design for expanding the polymer intermolecular interactions. (c) Ion concentration polarization (ICP)-based electrokinetic systems integrated with an ion-selective membrane.

3.2. Enhancing Molecular Selectivity in IEM by Membrane Functionalization.

IEMs are critical for electrodialysis and a diverse range of separation areas, including seawater desalination, wastewater purification, and resource recovery, as shown in Figure 5a. Despite the advances in IEMs with high monovalent/divalent inorganic ion permselectivity, a precise separation between ions having a similar (hydrated) radius or charge valence is challenging. In addition, commercial membranes still show limited permselectivity toward more complex mediums containing both organic species and inorganic ions in high concentrations, despite advances in the desalination of highly saline effluents.[80] Various approaches for functionalizing IEMs have been demonstrated to enhance permselectivity across inorganic species, multicomponent mixtures, and a mixture of inorganic and organic molecules.

Membranes can be functionalized through diverse techniques such as the layer-by-layer (LBL) assembly of cationic/anionic polyelectrolytes,[81] in situ polymerization of conducting polymers,[82] chemical modification,[83] and ionic dendrimer coating,[84] among others. The LBL method is one of the most prevalent modification approaches for separating monovalent from divalent ions by increasing the repulsive force acting on multivalent ions and facilitating the hydrophilic pathways to expedite monovalent migration.[85,86] Due to its facile synthesis and various adjustable parameters (e.g., polyelectrolyte characteristics, number of layers, different terminating layers, and preparation conditions) that can modulate the surface physicochemical properties, LBL functionalization has been integrated into several applications and architectures.[86−88]

Since electrostatics is the primary driving mechanism in LBL membranes, achieving precise separation between ions having the same valency remains challenging due to similar electrostatic interactions with the membrane. To overcome this limitation in monovalent selectivity, biomimetic membranes have been investigated to mimic the structure and transport mechanism of a natural potassium ion channel with a superior K^+ ion permeability (10^8 ions s^{-1} per channel) and monovalent ion selectivity of as high as 10^4.[89] As shown in Figure 5b, charged membranes embedded with porous crystalline organic salts as a selectivity filter demonstrated ultraselective K^+ transport (K^+/Li^+ = 363 and K^+/Na^+ = 31).[90] Synergistic effects of electrostatic and cation−π interactions imposed a higher transport energy barrier for Li^+ and Na^+, leading to a much higher K^+ permeability. Monovalent anions, such as Cl^- and NO_3^-, are also difficult to separate with commercial anion-exchange membranes (AEMs) and functionalized membranes.[91] In this regard, the zwitterionic membrane showed high selectivity among monovalent anions,[92] suggesting a potential direction to tune the ion interactions to achieve higher permselectivity.

Many IEMs for electrochemical separation systems have been designed for inorganic ions and have been studied with relatively simple binary or ternary mixtures. However, in practical biomanufacturing and fermentation processes, value-added organic species such as proteins and organic acids are often present in much more complex mixtures, in the presence of multicomponent inorganic and neutral molecules.[93−95] There is a lack of comprehensive research focused on their recovery from multicomponent mixtures or organic species. Recently, an LBL multilayer-modified AEM was integrated into a redox electrodialysis platform to selectively separate organic acids, such as succinic acid (Figure 5c).[5] This functionalized membrane allowed the complete rejection of negatively charged organic acids, regardless of their charges, from a complex ion mixture of model fermentation broth while maintaining the overall permeability of inorganic anions. The result was attributed to the combination effect of electrostatic repulsion and the size exclusion of large organic acid anions.

The membrane selectivity toward organic ions from inorganic ions can also be tuned by the molecular design of the ion exchange groups. Polysulfone AEMs functionalized with imidazolium groups have exhibited notable permeability toward organic compounds, exhibiting about 20-fold and 5.8-fold increases in permeability for lactate[96] and *p*-coumaric acid,[97] respectively, in comparison to quaternary ammonium-based AEM. AEMs functionalized with the guanidinium group, which can specifically bind to phosphates, facilitated the transport of phosphate and citrate anions compared to unmodified AEM.[98] Nonetheless, previous work has mostly focused on the separation of organic molecules from inorganic salts. The fractionation between organic species remains challenging due to the fouling susceptibility of IEMs, the relatively bulky sizes of valuable species, reduced ion mobility, and their sensitivity to pH variations. Moving forward, a more comprehensive understanding of the intermolecular interaction between functional groups on the membrane and individual organic species, the speciation of organic molecules, membrane morphology, and hydrophobicity characteristics of organic species is critical to achieving effective partitioning within value-added organic compounds.

4. CONCLUSIONS AND OUTLOOK

Driven by the increasing emphasis on energy efficiency and sustainability, electrified separation methods have expanded their scope to encompass a diverse array of applications including desalination, the recovery of valuable compounds, and the removal of emerging contaminants. In particular, polymer-functionalized interfaces play an important role in enabling selective adsorption and enhancing membrane selectivity. Despite significant progress in modulating selectivity through judicious polymer design, there are still major fundamental challenges that need to be addressed, including a comprehensive understanding of molecular-level interfacial bindings as well as advancements in electrochemical separation systems and polymer synthesis. Here, we present strategies to mitigate these challenges and explore future research directions for advancing selective electrochemical separations.

4.1. Comprehensive Understanding of Complex Molecular Binding Mechanisms. In both electrosorption- and membrane-driven electrochemical systems, the contribution of individual surface interactions to ion selectivity often remains unknown. While numerous experimental studies have highlighted the significance of electrostatic interactions, surface charge density, and surface morphology, a more detailed understanding of the molecular-level behavior is essential to advancing the development of a more accurate ion separation platform as suggested in Figure 6a.

On the experimental front, delving into operando analytical techniques, including the electrochemical quartz crystal microbalance,[99] spectroscopy,[39,100] and neutron reflectivity,[101,102] will provide valuable insights into elucidating the solvation effect, transient ion retention, structural changes of polymer films, surface interaction, and binding affinity. Beyond experimental interpretation, multiscale modeling of physicochemical interactions between target species and functional groups has been studied to understand selectivity and stability.[103,104] Density functional theory (DFT) and molecular dynamic (MD) simulations are two primary computational tools to deconvolute molecular interactions and binding mechanisms at the molecular level,[24,55] while numerical simulations through COMSOL and the response surface model elucidate the influence of operating parameters on the performance.[105−107] We believe that the multidisciplinary combination of molecular simulations and operando analytical techniques for interfacial interrogation can greatly contribute to achieving a comprehensive understanding of separation performance and eventually predictive control over polymer structures and their function.

Moving beyond selectivity within small inorganic species, we envision the electroseparation of charged metal complexes, organic compounds, and even biomolecules when they interact with membranes or redox-responsive polymers. For example, in the case of biomacromolecules such as proteins, multiscale modeling may be needed due to the larger length scale of the interactions with polymer interfaces and the presence of a differential surface charge distribution. Thus, we believe that a detailed understanding of more complex binding mechanisms can extend the scope of the target species for electrochemical separations.

4.2. New Synthetic Approaches for the Selective Functionalization of Redox-Active Groups. The development of more selective and efficient electrochemical separations benefits from the design and synthesis of new functionalized redox-active compounds. From a synthesis perspective, the restricted number of redox groups and their exclusive utilization for anions are two major challenges, particularly in the context of electrosorption. To mitigate these synthesis challenges, extensive research has been dedicated to multiresponse polymers, aimed at broadening the applicability of redox-responsive polymers along with the enhancement of electrochemical stability, selectivity, and switchability of the molecules. In addition to the redox responsiveness, these polymers incorporate extra features for regulating polymer reactivity such as optical responsivity, pH sensitivity, and hydrophobicity by tailoring the non-redox-active moiety, the hydrophilicity of counterions, and polymer chain lengths (Figure 6b).[108−113] Use of the intrinsic properties of polymers, including thermoelectric properties[114] and thermoresponsiveness,[115−117] could serve as additional pathways for fine-tuning selectivity and reversibility.

Going forward, we envision that organometallic compounds, particularly ferrocene- and cobaltocene-based systems, will continue to play a leading role as building blocks for redox-active polymers in electrochemical separations. The versatile nature of ferrocene and cobaltocene and their reversible redox properties have positioned these metal sandwich complexes as favored electrode materials in electrochemical separation processes.[118,119] From a synthesis perspective, the composition and core structure of these organometallic compounds bring several advantages, such as economic feasibility, high stability, and distinctive structural characteristics. Iron and cobalt exhibit an ideal combination of chemical properties (e.g., atomic radius and electron distribution) that ensures high stability for ferrocene and cobaltocene, as they fulfill the 18-electron rule.[98,120,121]

In particular, the abundance and cost effectiveness of iron confer a substantial advantage to ferrocene over other metallocenes, especially in the context of large-scale production and industrial applications. Ferrocene is well known for its diverse reactivity, exhibiting a vast repertoire of chemical transformations ranging from classical reactions to the most challenging topics in synthesis today.[122] The incorporation of one or more substituents at specific positions of the cyclopentadienyl ring holds significant research interest for enhancing the conformational effect and providing additional binding sites. In this regard, C−H activation in ferrocene is an emerging topic in the literature,[123] especially from the establishment of new methodologies aimed at solving remarkable problems related to selectivity in the synthesis of disubstituted ferrocenes.[124−127] Nowadays, these carbonyl derivatives can be prepared through selective C−H activation protocols, which employ milder reaction conditions and offer better functional-group tolerance. The recent work on the synthesis of 1,3-disubstituted ferrocenes via an enantioselective relay remote C−H activation strategy provides a good overview of the progress achieved in this field.[128] The envisioned catalytic cycle for the proposed reaction begins with an enantiodeterminant activation of C−H at the C2 position, facilitated by an inexpensive and readily available ligand. Subsequently, a palladium relay enables the reaction on remote position C3, governed by the insertion of a bridgehead-substituted norbornene.

In addition to ferrocene-based redox polymers, polymers incorporating cobaltocene have been extensively explored as selective electrosorbents[23,119] and stable anion-exchange membranes.[129] The fast electron transfer and electron-rich characteristics of cobaltocene have shown its capability in enhancing the uptake of long-chain PFAS as a working electrode.[23] Moreover, coupling cobaltocene-based polymers with PVF serves to effectively mitigate water electrolysis during electrosorption, addressing a major challenge in enhancing both selectivity and charge efficiency.[119] This integrated approach in the field of redox battery technology has been recognized as a potential future battery material, attributed to its remarkable power density and stability.[130] Particularly noteworthy is its distinctively low formal potential (typically $E_{1/2}$ ← 0.8 V vs Ag/AgCl depending on non-redox-active groups), leading us to envision cobaltocene, much like ferrocene, as a versatile organometallic compound with extensive potential for applications in selective separations and membrane materials.

In essence, the key to differentiating target molecules from those with similar structural or physicochemical properties lies in the enhancement of the conformational effect, specific interactions, and redox responsiveness. In this regard, it is worthwhile to investigate the impact of different copolymerization methods on the performance of selective separation. For instance, there are promising avenues for exploring the physicochemical properties associated with copolymer microstructures, including block copolymers, statistical copolymers, and gradient copolymers, and their corresponding effects on selectivity. Furthermore, from a synthesis standpoint, the central aspect of transitioning from a proof-of-concept study to industrial applications involves the advancement of more intricate synthesis approaches that employ cost-effective catalysts and simple separation steps. We believe that progress in synthesis methodologies and the development of versatile redox polymers will broaden the classes of redox-active materials, thereby tackling increasingly complex and challenging separations.

4.3. Molecular Selectivity in Electrokinetic Separations. Electrokinetic separations rely on the application of an electrical current to achieve the continuous separation of a desired species in response to an applied electric field rather than requiring sequential adsorption and release processes. Electrodialysis (ED) stands out as one of the well-established and highly effective electrokinetic separation methods and is particularly renowned for its successful application in desalination processes. However, ED membranes often do not afford much selectivity within the same charged species and are prone to fouling. Consequently, ongoing research actively explores the surface modification of existing membranes and the development of novel ED membranes,[131] encompassing various electrokinetic architectures such as redox-mediated ED,[5,45,132] shock ED,[133,134] and microscale electrokinetic separation techniques using ion concentration polarization (ICP).[135]

One strategy to address fouling is leveraging ion concentration polarization (ICP) through a combination of electrokinetic and convective forces, as illustrated in Figure 6c. ICP was initially studied at microchannel−nanochannel interfaces,[136−138] where electrical double layers overlap within a nanochannel and the channel transmits only cations while precluding the anion transport. Upon an applied potential, the nanochannel becomes a selective pathway for ions, carrying almost all of the current by a single ion type, resulting in the formation of an ion depletion zone (IDZ) at one end and an ion enrichment zone at the opposite side. The decreased number of charge carriers within the IDZ leads to the increase in solution resistivity and a locally enhanced electric field, which offers a method for separating charged species.[135] Unlike conventional ED, ICP-based techniques allow the simultaneous separation of inorganic ions and larger charged species due to the separation occurring along an IDZ rather than through a membrane with size exclusion properties. Thus, ICP-based techniques have been demonstrated for separating anions and cations with analytes as diverse as inorganic ions, biomolecules, cells, microplastics, and even neutral species.[139,140] More recently, IDZs have been integrated with ion-selective membranes such as Nafion and bipolar electrochemistry to avoid complex nanochannel fabrication (Figure 6c).[139,141] Regardless of the mechanism giving rise to ICP, the separation occurs on-demand only upon application of a sufficiently large potential bias.

ICP separation techniques often face a substantial scale-up challenge due to their reliance on microscale electrokinetic phenomena, which results in low volumetric throughput (on the order of nL/min). An emerging electrokinetic-based separation technology, referred to as shock ED, is showing great promise for a variety of water purification applications and providing a solution to this scaling-up problem by incorporating charged microporous media (e.g., silica glass frit) into the device architecture.[133,134] Importantly, a network of charged microstructures can create larger IDZs that may provide a roadmap for scaling up ICP-based electrokinetic separations. Moreover, shock ED is not as susceptible to membrane fouling as conventional ED because separation occurs at an IDZ interface rather than through a membrane. Selectivity for multivalent ions and heavy metals has been recently demonstrated, showing potential applications including the selective removal of low-abundance toxic heavy metals such as Pb^{2+} from drinking water.[32,142−144]

To date, a majority of ICP-based electrokinetic separations have focused on generating selectivity through a sharp concentration gradient throughout the flow channel to IEMs or porous electrodes. While emerging ICP electrokinetic separation techniques hold great promise, future explorations into how these devices operate with complex real-world matrixes are needed to enable scale-up. We believe that, going forward, surface functionalization and polymer design can enhance the selectivity for electrokinetic separations, broadening their applicability to multicomponent separations.

4.4. Electrochemical Engineering and Translation to Practical Deployment. To ensure applicability across a wide range of industrial scenarios, there is an urgent need to study, improve, and benchmark the mechanical, thermal, and chemical stabilities of redox-responsive polymers and ion-selective membranes. Within the context of membrane-integrated systems, the water splitting reaction under high current density significantly changes the solution pH by producing H^+ and OH^- ions. This abrupt pH shift can result in damaging the acid-/base-labile functional groups on the membranes or polymer electrodes, potentially compromising their selectivity. Therefore, it is essential to take into account the electrochemical reactions of ions or the conditions of the electrolyte, including Cl^- oxidation to Cl_2 which is then converted to hypochlorous acid (HClO) in water. The HClO can cause degradation of the functional groups and chain scission of the polymer backbones, deteriorating the mechanical stability of the membrane. Therefore, ion-selective membranes for electrochemical separation should be designed to be resistant to such potential parasitic reactions, in addition to the effort of the system design for extending membrane stability, as shown in the redox-ED system.

As emphasized throughout this Perspective, engineering of the electrochemical systems is as important as tailoring the molecular interfaces for industrial implementation and for achieving economically feasible translation to practical use. From a systems perspective, the considerations include the number and assembly of the flow channels, optimization of the operating conditions (e.g., batch/continuous modes, parallel/series connections, and constant voltage/constant current operations), and the integration of greener energy sources (e.g., solar panels,[145] waste-heat sources,[31,45,146,147] and photoelectrochemistry[71,148]). Life cycle assessment (LCA) and technoeconomic analysis (TEA) are also indispensable tools for assessing the feasibility of system designs toward practical translation. For example, TEA studies and experimental analyses have identified the use of IEMs in electrochemical separation systems as a potential bottleneck due to cost and susceptibility to fouling. Consequently, there is a growing trend toward exploring more cost-effective membranes in membrane-integrated systems.[45,149,150] Finally, in the long term, it is essential to establish accurate correlations and mathematical models to facilitate the translation from laboratory-scale to pilot-scale and even industrial-scale systems. The long-term aim is to establish a general, interconnected design framework from the molecular to the systems level to rapidly develop and deploy electrochemical separation processes for the constantly emerging and evolving global challenges in energy, the environment, and sustainability.

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Notes

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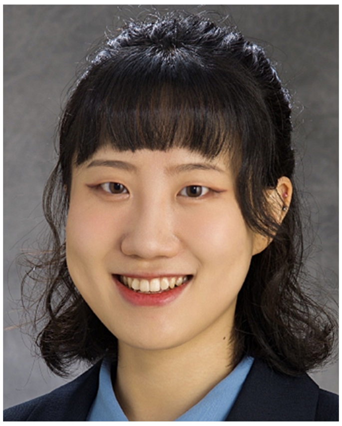
Biographies



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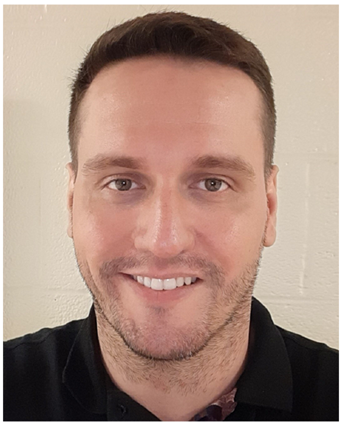

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