



State-of-the-Art perspective

Redox-electrodes for selective electrochemical separations



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ABSTRACT

Redox-active materials hold great promise as platforms for selective liquid-phase separations. In contrast to capacitive electrodes that rely purely on double-layer charge for deionization, redox-modified electrodes can be used to control Faradaic reactions at the interface to selectively bind various charged and uncharged molecules, thus modulating surface interactions through electrochemical potential solely. These electrodes can be composed of a range of functional materials, from organic and organometallic polymers to inorganic crystalline compounds, each relying on its own distinct ion-exchange process. Often, redox electrochemical systems can serve as pseudocapacitors or batteries, thus offering an advantageous combination of adsorption selectivity and energy storage/recovery. This review summarizes redox-interfaces for electrosorption and release, outlines methods for preparation and synthesis, discusses the diverse mechanisms for interaction, and gives a perspective on the future of redox-mediated separations.

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Contents

1. Introduction	6
2. Faradaic processes for deionization	7
3. Faradaic processes for electrosorption	8
3.1. Cations	9
3.2. Anions.	11
3.3. Specific chemical interactions	13
4. Synthesis and preparation of redox-electrodes	15
4.1. Redox-active organic conducting polymers	15
4.2. Redox-active organometallic surfaces.	16
4.3. Composites of conductive materials and redox-active species	16
4.4. Inorganic conductive electrodes: Metal-oxides and crystalline clusters	17
5. Perspective: chemical specificity and energy recovery.	17
5.1. Challenges in ion-specific separation: cost, selectivity and diverse applications	17
5.2. Energy integration: battery and pseudocapacitive separation systems	18
6. Conclusions.	18
References.	18

1. Introduction

Faradaic processes are at the core of many electrochemical applications, from electrocatalysis and sensing to energy storage. An

electrocatalyst transforms substrates into value-added products by promoting electron transfer through changes in its oxidation state. Electrochemically-responsive receptors rely on shifts in the oxidation or reduction potential to monitor chemical identity and concentration of target analytes [1]. Redox reactions accompanying ion intercalation govern charge/discharge potentials and rates in batteries [2–4]; and provide pseudocapacitance in addition to the usual double-layer capacitance for improved energy storage performance [5]. For all these

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applications, redox species at the interface of the solid electrode interact with ions in solution, be they supporting electrolytes or specific target analytes.

Molecular recognition in particular has been the principal application in which the goal is to enhance selective binding of solutes [1,6]. Target analytes for electrochemical redox-responsive receptors have ranged from ions to neutral species and even particles and biomacromolecules. The interaction of analytes in the liquid phase is coupled with voltage and current responses from the redox-components, which can be either molecular species in homogeneous solution or redox-species immobilized on the electrode interface, thus allowing for identification and quantitation in nanomolar concentrations [7].

Selective binding activated by redox reactions can go beyond sensing – heterogeneous redox-species can impart selectivity and act as electrochemically-modulated adsorbents for ion-extraction processes from the liquid phase, where ion capacity, selectivity and kinetics are all major design components for a successful electrochemical separation process. The large focus of recent electrochemical separations has been on deionization problems with carbon-based materials reliant on double-layer charge, in which ion-selectivity, though desirable, is neglected in favor of total ion capacity. Redox-modified electrodes, on the other hand, offer an opportunity to enhance selectivity for selective ion-separations and, in some cases, even increase ion uptake over high surface area carbon-based materials.

In terms of the fundamental science of ion-doping, electroactive organic and organometallic films have been used for binding various cations and anions selectively and reversibly through ion-exchange since the early 80s. Many of these studies have focused on the basic electrochemistry of the conducting polymers, which have resulted in a greater understanding of ion transport and redox-binding mechanisms. Over the past decade, with developments in high-surface area electrodes for energy storage, there has been renewed interest in redox-materials for ion-separations in practical applications. Charged molecules have been the prime targets for these earlier redox systems due to their electrostatically-driven attraction, such as electrochemically switched ion-exchange systems (ESIX) developed at the Pacific Northwest National Lab [8,9] to target cationic pollutants in waste streams [10–12]. More recently, battery and hybrid-type deionization processes have taken advantage of Faradaic-type electrodes to improve desalination efficiency [13]. The combination of surface polarization and redox activity enables binding with higher selectivity and faster kinetics than observed with traditional, solvent-based chromatographic methods. The inherent reversibility of the redox reaction allows for efficient recovery of adsorbed molecules without the need for extra solvent or change in the liquid-phase conditions [14].

In redox separation systems, selection of the appropriate materials chemistry for the electrodes is of paramount importance for successful electrochemical and separation performance. Fortunately, the explosive growth in the development of redox-active materials from various fields offers a large library from which to choose and improve, ranging from fully organic to pure metal electrodes. In particular, the discovery and implementation of innovative binding mechanisms is at the core of the development of next-generation redox-electrodes for selective separations. In this case, the task of designing proper binding mechanisms can benefit greatly from developments in molecular sensing and recognition. The targeting of specific, high-value or high-risk analytes, both organic and inorganic, in dilute concentrations is of crucial concern to chemical industries as well as environmental remediation. Some examples include organic synthesis products such as pharmaceuticals or commodity chemicals, which are highly desirable to target over buffers and background ions, or heavy metal cations such as mercury and arsenic from industrial waste. Chemical interactions based on donor-acceptor interactions or dispersion and hydrophobicity are but some of the binding mechanisms which can be designed into a redox electrode and applied for electrochemical separations.

In the current review, we summarize the application of redox-electrodes for electrochemical separations, both in deionization and selective electrosorption of ions. We discuss both the inorganic crystalline electrodes used for cation exchange as well as the range of polymeric organic and organometallic materials used for ion-doping, and present some novel developments that exploit chemical interactions for ion-selective extraction and release. We also review broadly the synthesis and preparation methods of redox-functionalized surfaces, and conclude by sharing perspectives for future materials and process design.

2. Faradaic processes for deionization

Water purification has been a key area of interest for researchers in electrochemical separations, due to both its scientific challenges and societal importance. New technologies are needed in order to address limited resources in many parts of the world, with water resources constrained by geography and affected by anthropogenic pollution [15]. A range of competing desalination techniques exist, mainly membrane-based such as reverse-osmosis (RO). With the development of high surface area conductive materials, electrochemical processes such as capacitive deionization (CDI) have narrowed the gap with membrane processes in terms of costs and energetic requirements [16–18]. In CDI, porous conductive electrodes are charged by applied potential and thus accumulate significant quantities of ions close to the electrode interface [15]. The mechanism for charging relies on the formation of an electrical double layer, with the electrodes acting as plate capacitors (Fig. 1a). CDI systems have the additional advantage of being able to store energy during the charging step, which can then be recovered during the discharge process. This serves to decrease the overall cost of the separation processes. Depending on the particular method, this energy recovery can range from 20% to 80% for membrane-capacitive deionization. One of the methods to increase performance is to utilize a cation/anion exchange membrane (Fig. 1b), which can serve both to select desired anions if required, but most importantly, to increase electrochemical performance by preventing cations from leaving the electrode-structure [17,19].

However, due to the electric field-based mechanism for charge accumulation in the double-layer, standard CDI technology does not provide an inherently high ionic selectivity. The presence of selective Faradaic reactions at the electrode similar to those in a battery material (Fig. 1c) can provide ionic-selectivity directly through chemical means. Ionic intercalation into inorganic matrices, which is at the core of battery technologies, is one of the most studied redox-processes in recent decades [20–23]. Redox-electrodes from battery-type materials can be designed for separation of salts, with the added selectivity that accompanies the intercalation reactions, which is the conceptual basis for battery desalination [24] (Fig. 2). Selectivity is desirable for a wide range of applications, such as chemical process purification from organic synthesis, or removal of particularly dangerous contaminants.

The main difference between these Faradaic-based systems and standard CDI processes, as noted, is that instead of the charge being stored in the EDLC, the charge is stored through the chemical reactions that occur on intercalation of the ionic species within the electrodes [24, 25]. In one of the earliest examples of a battery-deionization system, the cathode was made of sodium-manganese oxide ($\text{Na}_2\text{Mn}_5\text{O}_{10}$) nanorods, while the anode was made of silver [24]. The separation system works by operating the two-electrode system under sea-water to produce fresh water, and releasing the captured salts to a brine stream to regenerate the adsorbent (Fig. 2). The cathode was found to be highly selective towards Na^+ through preferential intercalation over other cations (Mg^{2+} , Ca^{2+} , K^+), and the anode was equally selective towards chloride over sulfate due to the more favorable reduction potential for the formation of the AgCl composite. The Coulombic efficiency of battery deionization (0.29 Wh L^{-1}) was reported to be comparable to that observed in reverse osmosis, making it a highly competitive desalination system.

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