



# Electrochemically driven adsorptive separation techniques: From ions to proteins and cells in liquid streams

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## ABSTRACT

Separation processes are of utmost importance for most industrial processes in the chemical, food, and pharma sectors. Electrochemical separation technologies gain more and more attention especially for the desalination of water, as they potentially lead to a reduction in the environmental footprint of the process. For salt, many different electrochemical desalination architectures and electrode designs have been proposed. Also other target molecules have been investigated, such as carboxylates, amino acids, proteins and whole cells. We note that the efforts are still scattered; therefore in this review we bundle and summarize the technological state of the art, and the application possibilities for capacitive as well as faradaic separation technologies for various targets. From this it is clear that there are still a lot of options that have been underused so far, and that electrochemical separation processes are key for the separation processes needed for a sustainable future.

## 1. Introduction

Numerous separation methods such as precipitation/crystallization, extraction, adsorption, and membrane filtration have been developed for purification of valuable products from liquid streams, or removal of impurities [1]. Based on theoretical evaluations, adsorptive separation is most efficient for the removal or isolation of minor components [2] and is commonly applied to remove pollutants (e.g. heavy metals) from water [3] or to isolate products of high value (e.g. proteins and peptides) [4,5]. It is also applied on very large scales, as for example in the separation of glucose-fructose [6], olefins and paraffins [7] or isomeric mixtures [8].

During adsorption a target molecule in solution first diffuses across a hydrodynamic boundary layer surrounding the stationary solid support, possibly followed by diffusion into the support, and finally by ad- and desorption to and from this interface [9]. Key factors for the ad- and desorption are the polarity and charge of the surface and target molecule (Van der Waals, electrostatic, hydration forces), whereas also complexation, ion exchange and microprecipitation can play a role [10]. Thus, different molecules in the liquid (mobile) phase have different affinities for the stationary phase and can either be physi-, chemi- or electrosorbed.

In most cases, adsorption is an exothermic process and desorption is

endothermic. For ions, typical adsorption energies to an ion exchange resin range between 0.6 and 25 kJ/mol, and the heat of adsorption can be as low as  $-24$  kJ/mol [11,12] depending on the charge of the ion and the substrate. If the adsorbent is more complex as in the case of proteins, multiple contact points in combination with structural rearrangements of the molecule lead to heats of adsorption as low as  $-1200$  kJ/mol at initial adsorption [13]. Other sources report binding free energies between  $-20$  and  $-50$  kJ/mol for individual amino acids [14], and interaction energies of  $-165$  up to  $-465$  kJ/mol for different protein-polymer surface combinations [15].

Surface interactions can be influenced by the temperature, pH, and ionic strength of the solution and for the product release by desorption, these environmental conditions need to be changed. In chromatography, this requires the use of extreme pH or ionic strengths (e.g. acidic or basic solutions or solvents) that may have a negative effect on sustainability of the process, and on the quality of the product. Recent innovations in “green chromatography” propose the use of stimuli responsive resins, that change their physical properties upon the application of other external stimuli such as temperature, pH, magnetic- or electric fields to improve separation processes [16]. Although this influences the ad-desorption part of the process, it does not influence the diffusion part, and that can be rather time consuming. In order to accelerate this, an additional driving force would be needed such as an electric field.

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In this review, we focus on the use of an electric field as stimulus in adsorptive separation processes, in which either capacitive or faradaic currents are used to store charged molecules in the double layer, or remove them, or to alter the stationary phase properties. Different technologies have been developed that make use of this concept: capacitive deionization, electrochemically modulated liquid chromatography (potentiostatic chromatography, elution voltammetry) [17–21], electrochemical solid phase (micro)extraction [19,20,22,23], and electrokinetic trapping [19] but the available options that could be envisioned are far from exhausted with this list. All these processes employ a surface to adsorb or immobilize the target molecules, and still a lot of progress can be made in terms of modulating the interactions occurring close to the surface, either through surface modification, or by influencing the interactions that take place at close range. Also, the full potential of different applications of these technologies is not tapped into yet. With this review we want to demonstrate the diversity of applications ranging from ions [24–26] to proteins [27–29] and cells [30].

To be clear, we exclude permeation based electrochemical membrane techniques such as electro-dialysis, electro-osmosis, electro-microfiltration and electrokinetic membrane extraction, and refer interested readers through to the following reviews [19,20,23,31–35]. Also electrophoretic techniques are not covered [36,37].

### 1.1. Surface interactions acting during electro-adsorptive processes

Interactions at the solid–liquid interface are key for adsorptive separation processes and the nature and strength of the interactions depend on multiple factors. For ions the dominant factor is the electrostatic interaction, but for larger molecules, the DLVO theory suggests that Van der Waals and electrostatic interactions are essential, and further hydration forces play a role [38,39]. Especially the latter two are strongly influenced by an electric potential applied to the interface, and are discussed in the next section. Van der Waals forces will not be covered since they are related to the dipole of the molecules in the surface and not influenced by the surface potential at low ionic strength [40], and thus cannot be used in a cyclic electrically driven adsorption/desorption process.

### 1.2. The electric double layer and electrostatic interaction energies

The charge as function of the distance to a charged solid wall is generally described with a double layer model. A widely shared view is

that the double layer consists of a concentrated layer of specifically adsorbed ions near the wall called the Stern layer, which becomes more diffuse when moving from the wall, and ultimately resembles the bulk electrolyte concentration far from the wall (GCS-model; Fig. 1a).

For solid interfaces that are electrically charged, the current involved in building the double layer is referred to as capacitive current: no electron is exchanged over the interface; charge is only accumulated [41]. The potential drop at an electrode interface can be modelled using the Debye screening length,  $\kappa^{-1}$  (Equation (1)) and the Poisson-Boltzmann equation (Equation (2)).

$$\kappa = \sqrt{\frac{2n_0e^2}{\epsilon\epsilon_0kT}} \quad (1)$$

$$\frac{d^2\psi}{dz^2} = \kappa^2 \frac{kT}{e} \sinh\left(\frac{e}{kT}\psi\right) \quad (2)$$

With a larger surface charge, the potential drop increases (Fig. 2a), and expands further. The electrostatic interaction energies between two charged plates at a finite distance from each other can be calculated using Equation (3).

$$V_E = - \int_{\infty}^D \left\{ 2n_0kT \left[ \cosh\left(\frac{e\psi}{kT}\right) - 1 \right] - \frac{\epsilon\epsilon_0}{2} \left(\frac{d\psi}{dz}\right)^2 \right\} dz \quad (3)$$

Like charges repel each other, while unlike charges attract each other upon approach, indicating the possibility for adsorption and desorption between the two plates. In Fig. 2c and d, the repulsion between two negatively charged flat plates is shown as a function of the distance  $D$  between the two plates, for constant potential and constant charge boundary conditions respectively.

Experimental studies to measure the double layer potential with open circuit and with applied potential have been done with atomic force spectroscopy [43–45]. At the potential of zero force, the size of the double layer is minimal but extends if the applied potential is shifted to more negative or more positive values, indicating an increase in ion storage capacity. Please note that the double layer for semiconductors (e.g. ITO) [46,47] is smaller compared to that of conductive surfaces such as gold [48–57], stainless steel [58], or pyrolytic carbon [59], since most of the potential drop occurs in the semiconductor layer itself [47].

In nanoporous materials such as activated carbon (<2 nm), the double layer is not fully developed, since the diameter of the pores is smaller than the distance over which the potential drops, and therefore

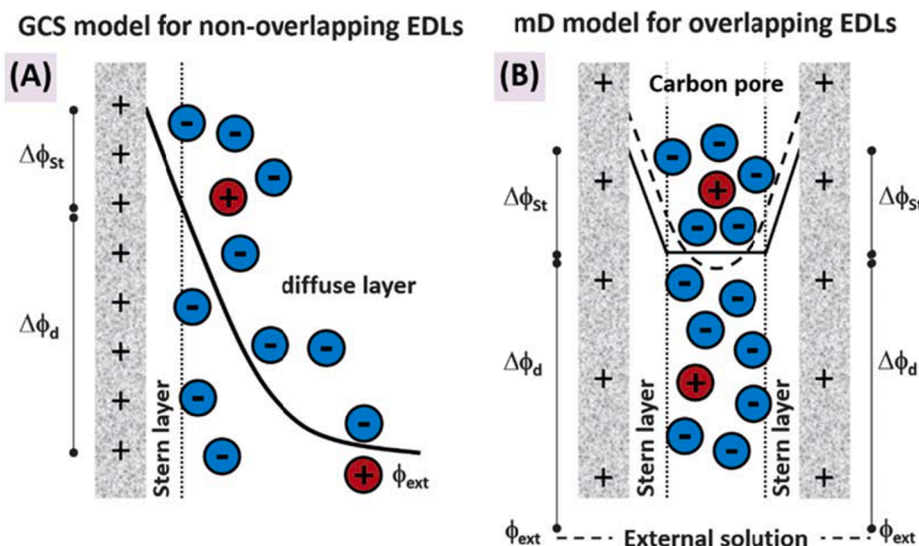
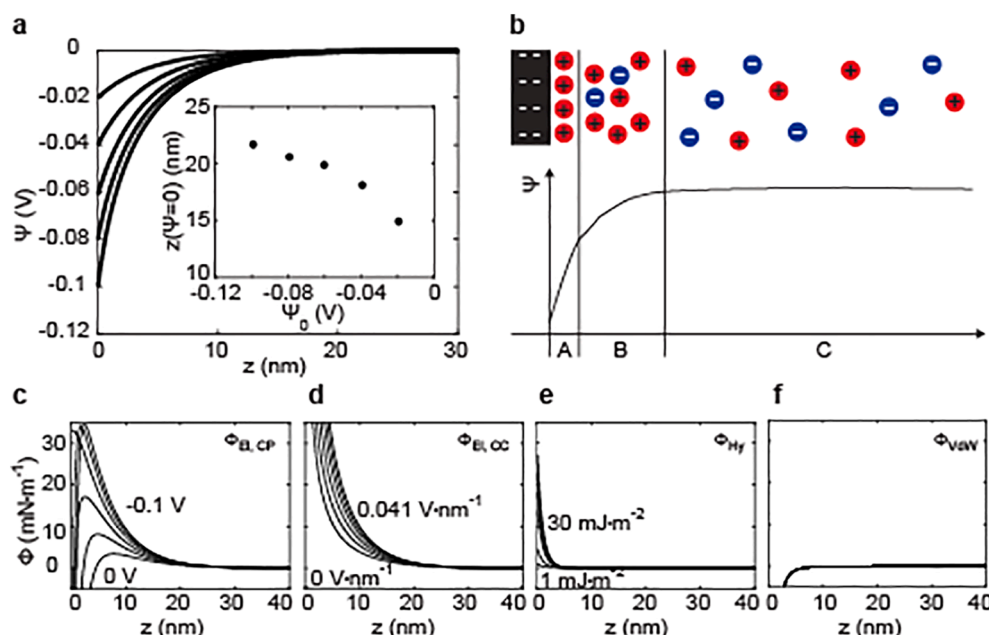


Fig. 1. Ion storage in a) non-overlapping (Gouy-Chapman-Stern model) and b) overlapping double layers (modified Donnan model). Reproduced from [25]



**Fig. 2.** (a) Double layer potential ( $\psi$ ) profile as described by the Poisson-Boltzmann equation with varying surface potentials ( $\psi_0$  between  $-0.1$  and  $-0.02$  V). Inset: Position at which the potential drops to  $0$  V (cutoff:  $-5 \times 10^{-4}$  V). (b) Schematic of the ion distribution at the electrode interface within the electric double layer and related potential profile. (c) Electrostatic interaction energy determined for constant potential boundary conditions; the gold electrode was held at  $0$ ,  $-0.2$ ,  $-0.4$ ,  $-0.6$ ,  $-0.8$ , or  $-1.0$  V, and the silica probe was set at  $-0.06$  V. (d) Constant charge boundary conditions were determined using Graham's equation for values between  $0$  and  $0.041$  V nm $^{-1}$  for the gold electrode and  $-0.0173$  V nm $^{-1}$  for the silica surface. (e) Hydration repulsion for a hydration repulsion amplitude between  $1$  and  $30$  mJ m $^{-2}$  with a decay length of  $1.3$  nm. (f) Van der Waals attraction for a Hamaker constant of  $5.7 \times 10^{-20}$  J. Reproduced from [42].

the double layers strongly overlap. In this case the structure can be described using the modified Donnan model (Fig. 1b). Further descriptions and summaries about the modified Donnan model can found in the following Refs. [25,60,61].

### 1.3. Hydration forces

As mentioned, hydration forces are important in ad- as well as desorption events, especially for macromolecules such as proteins in an aqueous environment [62]. Hydration repulsion can be attributed to primary, secondary, and structural hydration forces (Fig. 2f), related to the water molecules that are directly bound to the interface and/or protein molecules, water molecules in ionic hydration shells, and steric effects due to the finite volume of the solvent molecules [39,63]. If the orientation and density of water molecules at the interface is different compared to the bulk distributions, the force to displace a water molecule by an adsorbing target molecule is impacted [64]. At the surface of an electrode, the orientation and density of water molecules can be influenced by the applied potential [65], and thus ad- and desorption of e.g. proteins can be influenced [42].

In bulk water, the hydrogen-bonding-to-dispersion-forces have a ratio of 70:30, which relates to a contact angle of  $63^\circ$ . A surface exhibiting a lower contact angle is denoted hydrophilic; a surface with a higher contact angle is hydrophobic [66]. This implies that hydration interactions can be measured using electrowetting [67], in which the contact angle is a function of the applied electric potential [66]. Usually, the contact angle and the Gibb's free energy decrease when a potential is applied, which implies that the work of water adhesion increases, indicative of more hydration repulsion.

### 1.4. Capacitive separation processes

#### Capacitive separation of ions (Capacitive deionization)

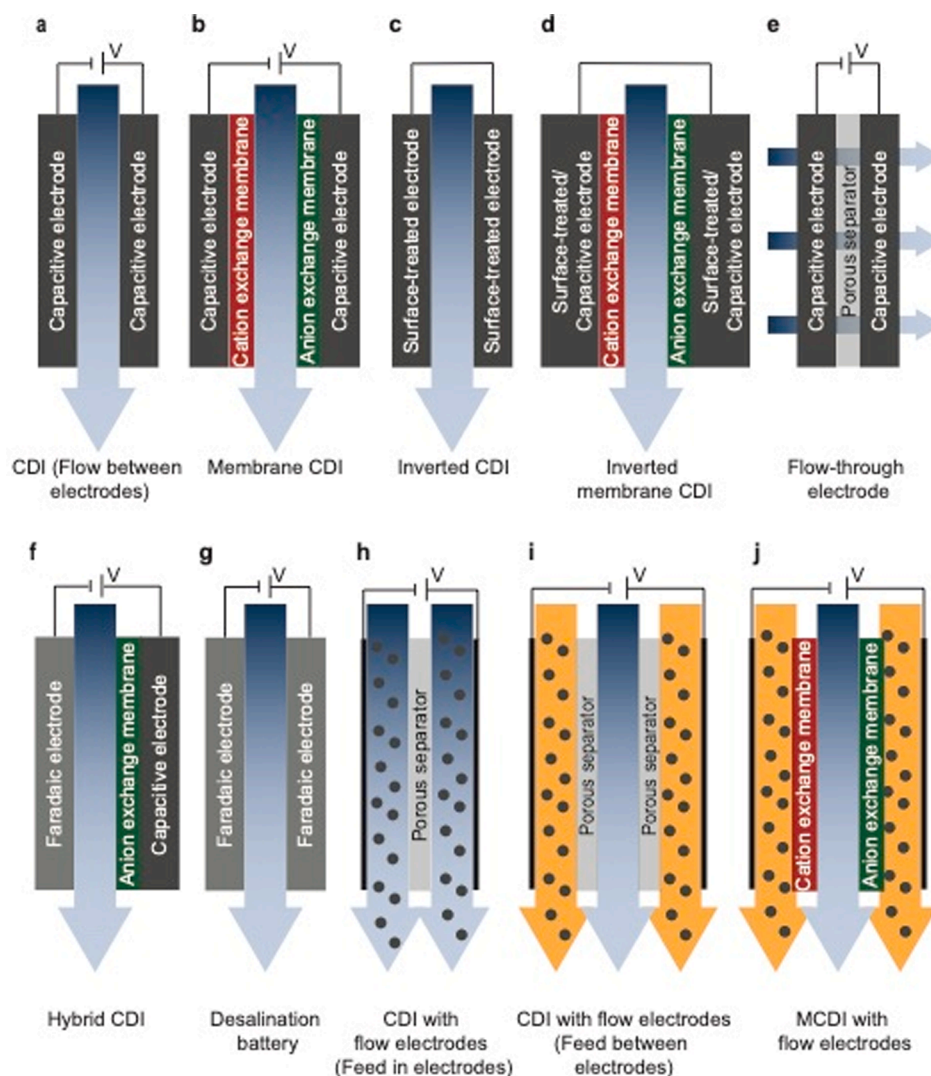
For ion separation, porous carbon materials are used in capacitive deionization (CDI) systems (Fig. 3). The most commonly used system contains two carbon electrodes opposite from each other, separated by a non-conductive spacer. The feed flows between the two electrodes through the spacer (Fig. 3a); while applying constant potential or current, charged ions dissolved in the feed are stored in the double layer at the electrode interfaces and thus the feed flow is desalinated. For regeneration of the electrodes the current or potential is reversed or

switched off, and the ions are released from the interface generating a brine [24–26]. Depending on the carbon material, electrosorption capacity values range from  $0.25$  for simple activated carbon to  $24.2$  mg/g in graphene aerogels [68,69] in which nanopores play a crucial role.

As an extension, CDI in flow-through mode, (Fig. 3 e) [70] or with carbon flow electrodes (Fig. 3 h-j) have been developed, and besides carbon intercalation materials are currently investigated to boost the desalination capability (Fig. 3 f-g). In these materials, ions are captured through redox reactions at the interface. Although Biesheuvel *et al.* [41] argue that this can be considered capacitive ion storage (the electro composition stays the same, and no electrons are transferred), we follow other reviews and discuss intercalation materials in the context of faradaic separation processes [71].

By inserting ion selective membranes (Fig. 3b) between the electrodes, [72] or coating the electrodes [73], the charge efficiency of flow between desalination processes can be improved, and the removal of specific ions such as nitrate can be promoted [74–76]. Furthermore, successful desalination of more complex feeds such as brackish water containing proteins [77] or micro-organisms [78], or even biomass hydrolysates containing sugars, organic acids or furans [79] have been reported. Besides,  $\text{ZnCl}_2$  was separated from insulin samples [80] while acetic and sulfuric acid was removed from hydrolysate [81]. Furthermore, it is good to mention that CDI technology on larger scale has been reported [82].

In contrast to conventional CDI in which adsorption takes place due to an applied potential or current, in inverted CDI, modified electrodes with additional surface charges (anode: net negative; cathode: net positive) are used to store ions (Fig. 3c). This means that adsorption occurs at  $0$  V [83,84] or the potential of zero charge [85], whereas desorption is activated by depolarizing the electrodes electrochemically. This saves energy during loading especially at higher solution conductivity, and allows for the selective adsorption of specific ions, depending on the groups present on the electrodes. For iCDI, in literature carbon materials modified with tetraethyl orthosilicate and/or nitric acid [83,84], or polystyrene sulfonate [86] have been used to increase the net negative charge, and the opposite charge was increased with ethylenediamine [84] or poly(diallyldimethyl-ammoniumchloride) [86]. Activated carbon electrodes were treated with cetrimonium bromide and sodium dodecyl benzene sulfonate for the selective removal of nitrate [87,88]. A theoretical overview of CDI desalination systems and the influence of chemical surface charges is available from Biesheuvel *et al.* [89].



**Fig. 3.** Capacitive deionization technologies ranging from flow-between (a-d, f, g) to flow-through (e) and flow electrode (h-j) set ups, using either capacitive or faradic ion storage principles. Modified from [25].

The efficiency of an inverted CDI process can be further increased by inserting ion exchange membranes, possibly in combination with unmodified and modified activated carbon electrodes (Fig. 3d). The separation performance of this inverted membrane CDI set up was competitive with conventional CDI using the same electrodes [86,90].

### 1.5. Capacitive separation of larger molecules

Capacitive current can also be used for adsorption of colloids and macromolecules (Fig. 4) as investigated using reflectometry, ellipsometry, or surface plasmon resonance equipped with an electrochemical cell (as summarized in Table 1). For example the adsorption of polyvinyl pyridine [91,92], poly(propylene imine) dendrimer [92], and of poly(vinyl imidazole) [56] (positive at low pH) increased with the cathodic potential. Thiols could be chemi- or physisorbed onto mercury depending on the applied potential [93], and AFM studies revealed attractive and repulsive forces at the positive and negative potentials, respectively, acting on negatively charged silica particles [57,94], and DNA [95].

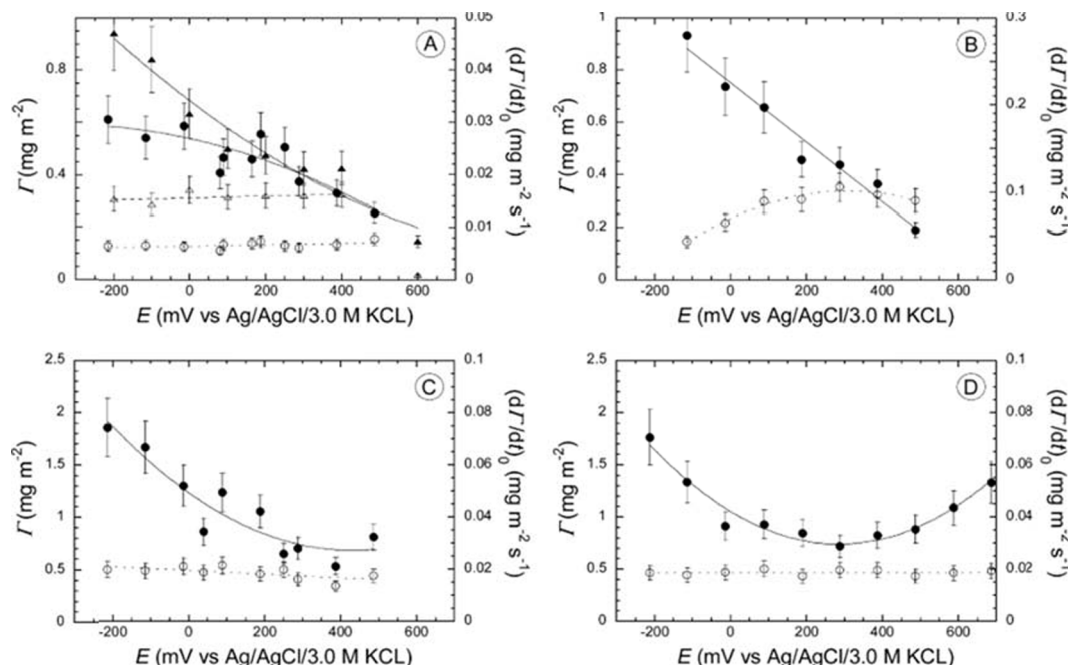
For the adsorption of blood proteins [54,58,59,96–98], lysozyme [92,99] and horseradish peroxidase [100] a similar trend was found: the adsorption increased with increasing potential relative to the protein charge. Desorption was only detected for DNA [101–103] and

$\beta$ -lactoglobulin [42]. Difficulties for desorption in other cases were mostly related to multiple contact points, effectively rendering the adsorption irreversible. Although mostly not considered, for an electrochemical protein separation process, the change in surface tension induced by the applied potential due to hydrostatic and electrostatic forces was important [42]. A first capacitive protein separation process was proposed by Fritz et al. (Fig. 5), ad- and desorption of whey protein isolate to and from various electrodes that may carry a polyelectrolyte layer could be controlled by an externally applied electric potential. Since protein ad- and desorption occurred at opposite potentials compared to salt ad- and desorption, this makes this process also useful for desalination of proteins (Table 2) [27].

### 1.6. Electrically responsive coatings (capacitive current)

Capacitive current may be used to trigger conformational changes in the surface coating, and thus to indirectly promote the exchange of larger molecules [16,104,105]. This was achieved by coating mercaptohexadecenoic acid at low surface coverage to a gold electrode (Fig. 6). At negative potential the hexadecenoic acid chain was oriented perpendicular to the surface, whereas upon positive depolarization the carboxyl group was directed towards the electrode surface and the chain folded upon itself. Hence, the nature of the surface changed from





**Fig. 4.** Adsorbed amounts (closed symbols) and adsorption rates (open symbols) of charged macromolecules to gold electrodes as function of applied potential. (A) PVP<sup>+</sup>, 12 k (b, O), concentration 1 mg/l, and 124 k (2, 4), concentration 5 mg/l, pH 6.4. (B) Adsorption of DAB-64 from a 5 mg/l solution at pH 6.9. (C and D) Adsorption of lysozyme from a 3 mg/l solution at pH 6.4 and pH 5, respectively. Background electrolyte 1 mM KNO<sub>3</sub>. The lines are to guide the eye. Reprinted with permission from [92].

negatively charged to hydrophobic, allowing the separation of streptavidin and avidin with isoelectric points of 5.8 and 10.5, respectively [106–109]. The same system was also used to retain and release bacteria [110]; and in slightly modified form using a terminal amino group [106] as well as positively charged oligolysine peptides instead of the carboxyl groups [111]. Zwitterionic phosphorylcholine was theoretically investigated; the charge ratio between the phosphate and choline group shifted as function of applied potential. This may change the interaction with Cytochrome c, indicating that ad- and desorption could be possible using a potential switch without impacting the structure of the protein [112]. Also, multi-component, self-assembled monolayers have been tested for cell adhesion, but this adhesion is irreversible [30]. For electrically responsive coatings, charged polyelectrolytes [113–115] such as polystyrene sulfonate [116,117] and pyridine [118] have been suggested.

### 1.7. Faradaic separation processes

In contrast to the capacitive separation processes, the storage of charged species in faradaic separation processes is based on charge transfer. Some argue that this includes the detachment of the reaction product from the electrode after electron exchange, and thus intercalation materials or redox-active electrode coatings would be capacitive [41]. However, here we maintain the classification used in previous reviews [25,120] and limit ourselves to processes that use electrodes at which redox reactions occur leading to the storage of target molecules.

#### Faradaic separation of ions

Partition chromatography of metal ions by electrodeposition was reported already in the sixties [17]. The distribution coefficient  $k_D$  between solution and stationary phase of Ti and Pb could be influenced by an applied electric potential (Nernst equation). As stationary phases, mercury [17], amalgamated nickel, lead, noble metals, as well as other amalgamated metals, and graphite [18] have been reported.

Through the development of intercalation materials for batteries and super-capacitors, the storage capacity could be greatly improved. This allowed ions to be stored within the electrode material and not only at

its surface. Especially for cation separation (lithium, sodium, potassium) many materials have been considered such as manganese oxide [121–123], iron-based phosphate [124,125], and hexacyanoferrate [126–128]. For chloride ions, silver and bismuth electrodes have been proposed [121,129,130] or two-dimensionally layered materials such as MXene [131] and MoS<sub>2</sub> [132,133]. Some intercalation electrodes can also be used for the selective removal of ions using specific conversion reactions or tunnel structure [123]. For reviews on intercalation materials we refer to the appropriate manuscripts [71,120,134,135].

Conductive and redoxactive polymers have also been considered for ion-exchange voltammetry, electrochemically modulated liquid chromatography [22,136–140], and as component in batteries [141], and pseudocapacitors [142]. As such, polypyrrole (Fig. 7 a and b) and polyaniline are neutral, but when partially oxidized at positive potentials they became positively charged; a negative potential returned the polymer into its neutral reduced state. This allowed the exchange of counter anions and electro-inactive analytes [19]. The ion selectivity of a polypyrrole electrode could be adapted by doping. Cl<sup>-</sup> doping led to the following preference: Br<sup>-</sup> > SCN<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > I<sup>-</sup> > CrO<sub>4</sub><sup>2-</sup>, whereas perchlorate doping changed the sequence to SCN<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > CrO<sub>4</sub><sup>2-</sup> [143–145]. Cations could be adsorbed by entrapping large anions into the polypyrrole and polyaniline electrode (Fig. 7b), since at reduced state the overall charge of the electrode was negative [146,147]. For this, anionic intercalation materials [148,149] have been discussed, and also catechol and quinones [150]. Other suggested conductive and redox active polymers were polyampholyte [151], sulfonate-ferrocene copolymer [151–153], poly(2,6-pyridinedicarboxylic acid) [154] or polythiophenes [155–158]. Over-oxidizing polypyrrole increased the preferential collection of cations over anions in the polymer matrix [159,160].

Metallocenes, bipyridines, porphyrines and other organometallic redox-active polymers were found to be interesting candidates for electrochemical separation processes, since electron-transfer rates and electronic structure of the metal–ligand system can be manipulated with an applied electric potential [135]. When the electrode was oxidized the metal became positively charged and thus stored ions reversibly. Several

**Table 1**

Overview of protein ad- and desorption in capacitive processes.

Target molecule	Medium	Electrode	Detection method	Ads. at OCP [mg/m <sup>2</sup> ]	Ads. at applied potential (vs. Ag/AgCl) [mg/m <sup>2</sup> ]	Des. efficiency	Ref.
Polyvinyl pyridine, 1–5 mg/ml	KNO <sub>3</sub> , 0.001 M, pH 6	Gold	Reflectometry	0.5	–200 mV: 0.8 600 mV: 0.2	–	[91,92]
poly(propylene imine) dendrimer, 5 mg/ml	KNO <sub>3</sub> , 0.001 M, pH 7	Gold	Reflectometry	0.5	–190 mV: 0.9 500 mV: 0.2	–	[92]
Poly(vinyl imidazole)	KNO <sub>3</sub> , 0.01 M, pH 3	Gold	Reflectometry	0.4	–400 mV: 0.8 600 mV: 0.4	–	[56]
DNA, 0.2 µg/ml	Phosphate buffer saline pH 7.4, 0.01 M	Silicon coated with amine-rich allylamine plasma polymer	Fluorescence microscopy	0.4	1000 mV: 1 –750 mV: 0.18	85%	[101]
Human serum albumin, 100 µg/ml	Phosphate buffer saline pH 7, 0.2 M	Gold	Radio labeling	2	–800 mV: 0.9 700 mV: 4	–	[54]
Human serum albumin, 5.26 mg/ml	NaCl, 0.15 M, pH 7.4	Platinum	Ellipsometry	2	639 mV: 5.5	–	[96]
Immunoglobulin G, 100 µg/ml	Phosphate buffer saline pH 7, 0.2 M	Gold	Radiolabeling	3	–800 mV: 2 700 mV: 4.5	–	[54]
Bovine γ-globulin, 11.4 mg/ml	NaCl, 0.15 M, pH 7.4	Platinum	Ellipsometry	6	839 mV: 12.5	–	[96]
Human fibrinogen, 3.2 mg/ml	NaCl, 0.15 M, pH 7.4	Platinum	Ellipsometry	6	539 mV: 14	–	[96]
Lysozyme, 3 mg/ml	KNO <sub>3</sub> , 0.001 M, pH 6	Gold	Reflectometry	0.8	–200 mV: 1.8, 400 mV: 0.5 700 mV: 1.4	–	[92]
β-lactoglobulin,	NaCl, 0.005 M, pH 6	Gold	Surface plasmon resonance	3	–400 mV: 1	12%	[42]
Avidin 0.1 mg/ml	PBS 10 mM, pH 7.4	Gold coated with mercaptohexadecanoic acid	Fluorescence labeling		–300 mV: 86 300 mV: 8	90.6%	[106]
Streptavidin 0.1 mg/ml	PBS 10 mM, pH 6.6	Gold coated with aminohexadecanethiol	Fluorescence labeling		300 mV: 75 300 mV: 4	94.6%	[106]
NeutrAvidin 0.037 mg/ml	PBS, pH7	Oligopeptide coated gold surface	Surface plasmon resonance	2300 relative response units	–400 mV: 200 rru +300 mV: 4000 rru	–	[111]
M. hydrocarbonoclasticus, OD600nm = 1	Artificial Seawater, 33.33 g/l pH8.2	Gold electrode with 11-mercaptopentadecanoic-acid coating	Surface plasmon resonance	2800 RU	289 mV: 800 RU –211 mV: 3000 RU	3 min: 83%, 5 min: 74%, 10 min 54%, Longer: irreversible	[110]
Bovine aortic endothelial cells, 10 <sup>6</sup> cells	PBS, pH 7.4	Silicon electrode with multicomponent SEM: GRGDS peptides, hexa(ethylene glycol) with ammonium end group	Fluorescence labeling + cell counting		300 mV: 5 Cell/mm <sup>2</sup> –300 mV: 90 Cell/mm <sup>2</sup>	–	[30]
Bovine aortic endothelial cells, 10 <sup>6</sup> cells	PBS, pH 7.4	Silicon with multicomponent SEM: GRGDS peptides, hexa(ethylene glycol) with sulfonate end group	Fluorescence labeling + cell counting		300 mV: 110 Cell/mm <sup>2</sup> –300 mV: 60 Cell/mm <sup>2</sup>	–	[30]

organo-metals based on for example Co [161], Os [162–164] or Fe [165–168] have been proposed for the separation of different anions, and in some cases cations (Fig. 7c). The combination of a poly(vinyl) ferrocene electrode and a poly-TEMPO-methacrylate also allowed the selective separation and oxidation of trivalent arsenic [169], and mercury could be remediated using a nanostructured poly(3-hexylthiophene-2,5-diyl)-carbon nanotube composite electrode [170].

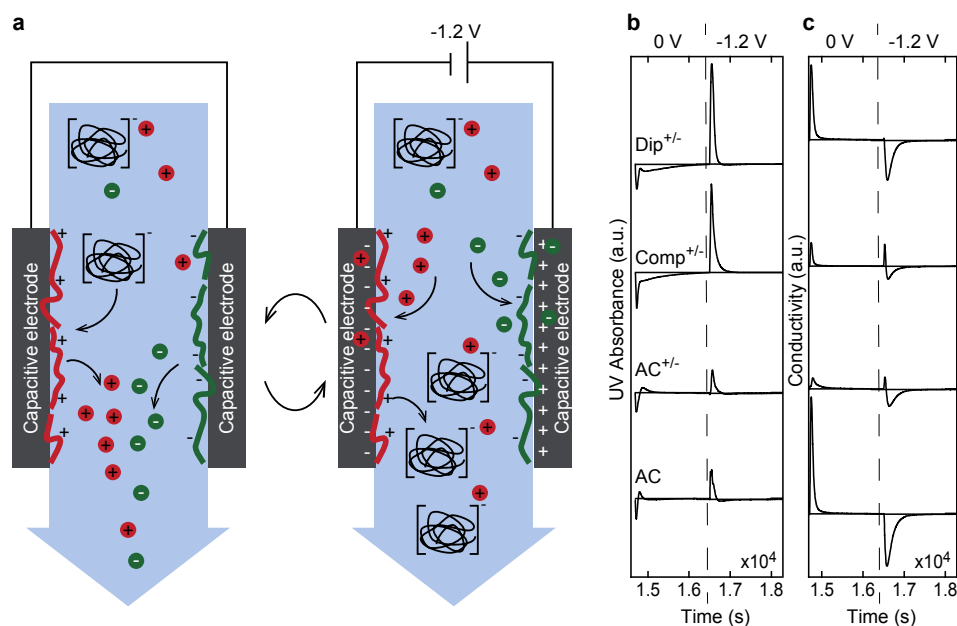
Ad- and desorption of ions can also be realized by electrochemically induced pH changes when using pH responsive coatings such as poly-4-vinylpyridine (Fig. 8a) [171]. In an aqueous environment, water splitting can be locally induced at potentials over 1.23 V, leading to a local change of the pH [172,173]. Redox couples such as quinon/hydroquinone [174–176] and anilin/hydroanilin [177,178] may serve as proton source or sink, and thus influence the pH and their storage properties (Fig. 8b).

### 1.8. Faradic separation of larger molecules

While most systems were developed for the separation of small ions,

some of the systems presented earlier have been used for ad- and desorption of larger molecules (chemical pollutants, proteins and cells: summarized in Table 3). Polyvinyl(ferrocene) functionalized carbon nanotube electrodes were reversibly oxidized and reduced, enabling good separation (separation factor > 140) of carboxylate, sulfonate and phosphonate [179]. Using the same approach, protein (lysozyme, myoglobin, horseradish peroxidase, ribonuclease-A, α-chymotrypsin, bovine serum albumin) ad- and desorption was realized (Fig. 9) [28].

Further, electro responsive polymers have been used, such as composites of poly(N-methyl pyrrolydinium) and poly(styrene sulfonate) onto which dopamin reversibly adsorbs at reductive potential [180]. The adsorption rate and adsorbed amount of glucose oxidase could be increased by applying a positive potential to a polyanion-doped polypyrrole film [181]. Molecular imprinting of overoxidized sulfonated polypyrrole (OSPPy) was used for the separation of L-glutamic acid (Fig. 10) [182], naproxene [183], salicylate [184] and fluoroquinolones [185]. Polythiophene electrodes (poly(3-dodecylthiophene) and poly(3-octylthiophene)) reversibly adsorbed neutral arsenobetaine that passively binds to the long hydrophobic allyl chains at open circuit



**Fig. 5.** a) Schematic of capacitive protein separation as described by Fritz et al indicating sequential protein and salt adsorption and release depending on the potential applied. Under open circuit potential salt is released and proteins are stored, whereas proteins are released and salt is adsorbed when the electrodes are biased. b) and c) showing the change of the UV absorbance (protein), and the conductivity (salt), respectively, for both phases, and for four different sets of electrodes [27].

**Table 2**

Overview of capacitive protein ad- and desorption processes.

Target molecule	Medium	Electrode	Process	Detection method	Protein ad- and desorption capacity	Salt ad-desorption capacity	Ref.
Whey protein isolate, 1.5 mg/g	NaCl, 0.005 M, pH 6	Activated carbon: polyelectrolyte composite	Inverted capacitive protein separation	Protein: UV sensor Salt: Conductivity sensor	10 mg/g	1 mg/g	[27]
Whey protein isolate, 1.5 mg/g	NaCl, 0.005 M, pH 6	Activated carbon with polyelectrolyte adlayer	Inverted capacitive protein separation	Protein: UV sensor Salt: Conductivity sensor	10 mg/g	3 mg/g	[27]

potential, with desorption triggered by the reversible oxidation of the polymer [186,187]. More recently the separation of perfluorinated compounds were demonstrated using a combination of redox-copolymers (4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl and 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine) [188].

When targeting protein or cell separation, it is important to avoid irreversible fouling of the electrodes, and thus, antifouling coatings were developed. For example, penta(ethylene glycole) groups were used as an antifouling layer, which could be modified with ligands specific for a protein or a cell. This ligand could then be linked to a redox active quinone protionic ester (Fig. 11). In this way, the target cell or protein could be captured by the ligand, and released upon applying a negative potential to reduce the quinone linker [189–193]. In a similar fashion, polyethylene glycol was used in combination with redox-active haeme groups for the reversible binding of  $\beta$ -lactoglobulin [194]. Interesting reviews on these systems are [20,195].

## 2. Methods to analyze ad- and desorption or macro molecules

To study the impact of electrode potential on ad- and desorption of macromolecules, such as proteins, different techniques were used. It was possible to indirectly measure the amount of adsorbed material through bulk fluid depletion; however one can also directly observe the amount of material adsorbed at a surface, using reflectometry or surface plasmon resonance. Further, with AFM the ad- and desorption forces may be quantitatively measured (Table 4). In the following section, we discuss

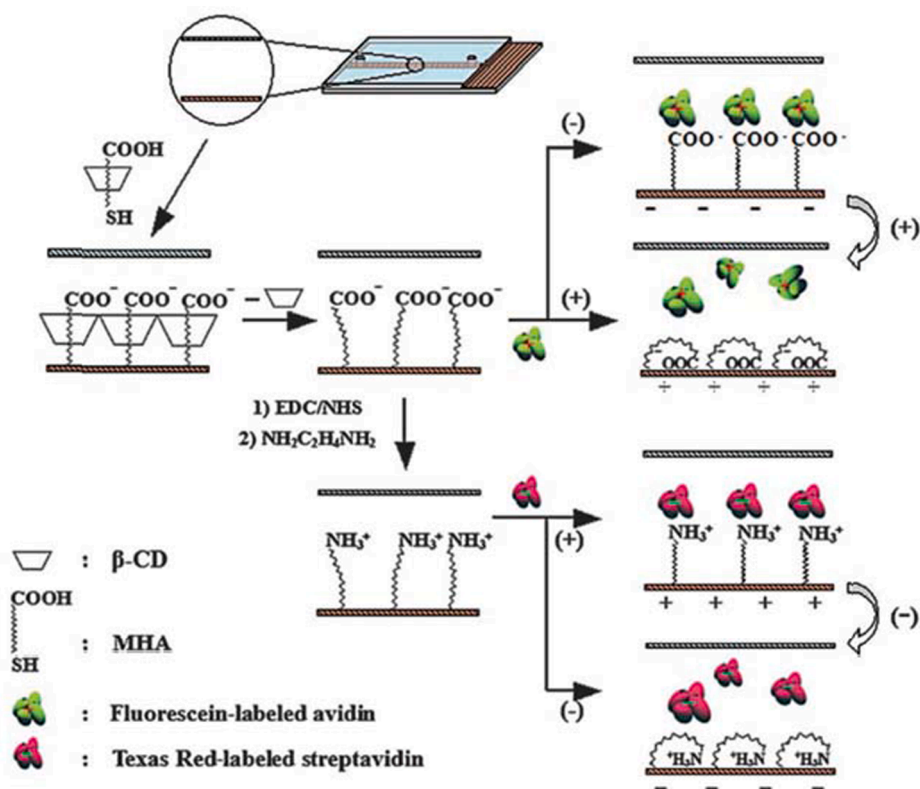
these methods (see also Table 1 and 3 for the respective references).

### 2.1. Indirect measurement through bulk depletion

Adsorption and desorption of macromolecules can be measured indirectly by tracking their concentration in the bulk solution e.g. by measuring the conductivity, UV absorbance [27], fluorescence, or by using target specific assays (e.g. Bicinchoninic acid assay [28,181], o-Phthaldialdehyde assay [181]). The sensitivity depends on the detection method, and sampling is sometimes difficult. Nevertheless, the clear advantage that this technique holds is that it is independent of the electrode material, meaning that any type of electrode and/or coating can be tested, also on large scale.

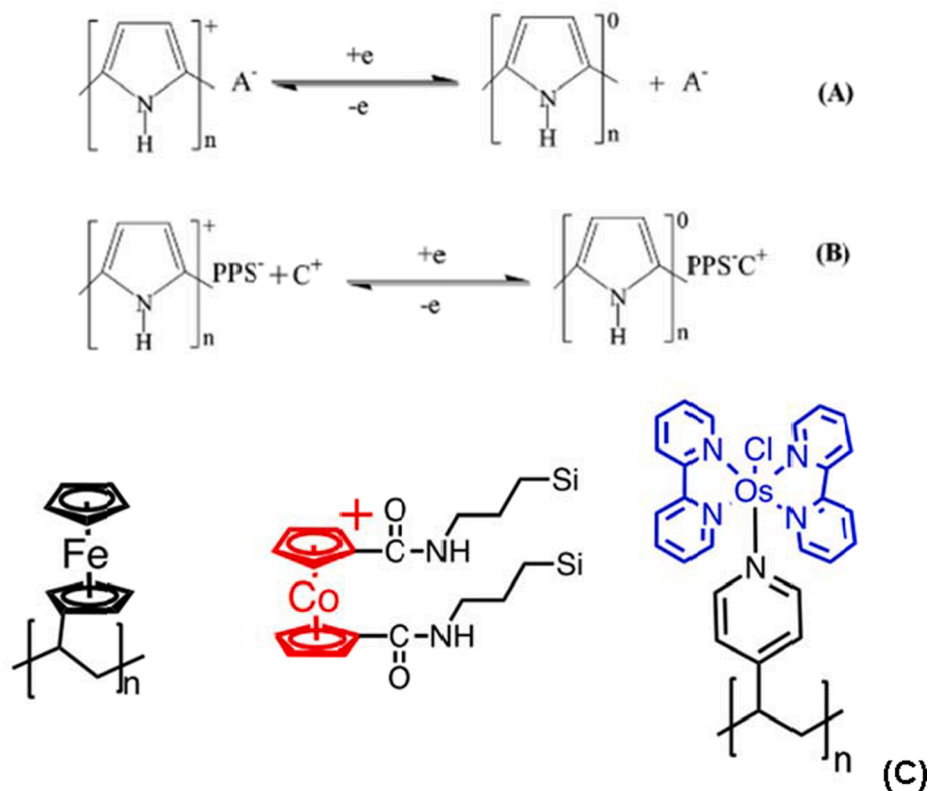
### 2.2. Direct surface adsorption measurement: Reflectometry

In reflectometry a laser is projected through a prism onto a planar silicon substrate, and the intensity of the reflected polarized light is measured, which can be related to the amount of adsorbed material through the refractive index. To increase the sensitivity of the method, usually a transparent silicon oxide layer is grown on top of the silicon. For electrochemically driven processes this was impractical due to the insulating properties of silica; therefore a gold coating was applied, in spite of it having a complex refractive index that reduces the signal intensity [91,196]. Gold surfaces can be easily modified via thiol bonds and have served as a basis for diverse polymer coatings. Other potential



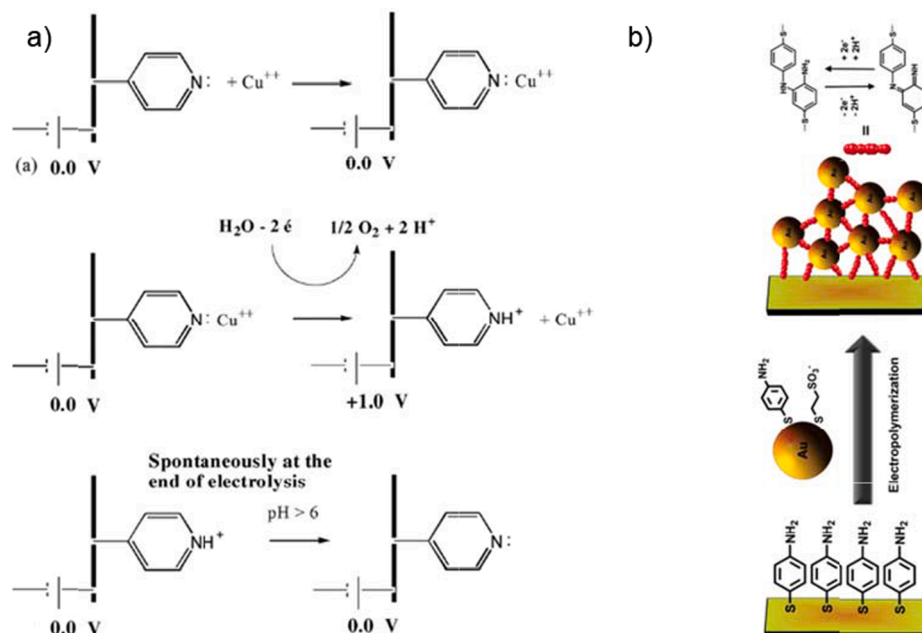
**Fig. 6.** Schematic representation of electro-responsive surface coating for protein separation using a flexible hydrophobic carbon back bone and a charged head group (either  $\text{COO}^-$  or  $\text{NH}_3^+$ ). Upon applying a potential, either the chain is upright, exposing the head group or bent, exposing the backbone. MHA: mercapto-hexadecanoic acid.

Reproduced with permission from [106]



**Fig. 7.** a) Redox reactions and ion exchange properties of polypyrrole films for a) anion ( $\text{A}^-$ ,  $\text{Cl}^-$  or  $\text{ClO}_4^-$ ) and b) cation extraction (PPS stands for polystyrene sulfonate) [137]. c) Examples of organometallics. (from left to right: Ferrocene, cobaltocene and osmium-bipyridine) [135].





**Fig. 8.** a) Electro-triggering of pH-switchable ligands: (top) capture step at low or zero potential, (middle) expulsion step at electro-oxidizing potential and (bottom) spontaneous restoring at low or zero potential [171]. b) Schematic representation of electropolymerization of bis-aniline-cross-linked Au NP composite, and generation of electrochemically induced pH changes in aqueous solutions. Reproduced with permission from [178]

**Table 3**

Overview of Faradaic protein ad- and desorption.

Target molecule	Medium	Electrode	Detection method	Ads. at OCP [mg/m <sup>2</sup> ]	Ads. at applied potential (vs. Ag/AgCl) [mg/m <sup>2</sup> ]	Des. efficiency	Ref.
L-glutamic acid, 10 mM	KCl-HCl buffer, pH 1.7	Overoxidized polypyrrole film on Pt coated quartz crystal	Fluorescence spectroscopy, (QCM)	13.5	$-350 \text{ mV}$ : 9 $600 \text{ mV}$ : 1.5		[182]
$\alpha$ -chymotrypsin, 1 mg/ml	Phosphate buffer, 50 mM, pH 7	poly(vinyl)ferrocene in carbon nano tube matrix	Bicinchoninic acid assay of supernatant	187		>95%	[28]
Streptavidin, 60 nM	Phosphate buffer, pH 7.4	Alkenethiol coating with quinone propionic ester and biotin ligand	Surface plasmon resonance	1.1	$-700 \text{ mV}$ : 0.055	95%	[191]
Glucose oxidase, 5 mg/ml	Phosphate buffer, pH 7	Polyanion polypyrrole film on aluminum sheet	BCA protein assay, QCM, o-phthaldialdehyde assay)	20	$1000 \text{ mV}$ : 60 $-400 \text{ mV}$ : 52		[181]

coatings are indium tin oxide or reduced graphene oxide [197], since both are conductive and have a lower complex refractive index compared to gold. Since the laser light has to travel through the electrolyte solution, this solution should be clear and thus may only contain components at low concentration.

### 2.3. Direct surface adsorption measurement: Surface plasmon resonance

In contrast to reflectometry, in surface plasmon resonance the laser is projected onto the back side of the electrode; the intensity of the reflected light depends on the generation of surface plasmons. At a certain angle of the incoming light, all energy is converted into fluctuation of electrons at the metal-electrolyte interface and the reflection is minimal. This so called SPR-angle depends on the refractive index at the interface and thus on the amount of e.g. proteins adsorbed. In SPR, mostly gold is used but also silver or graphene coated substrates have been applied. [198,199]

### 3. Measuring adsorption forces: Atomic force spectroscopy

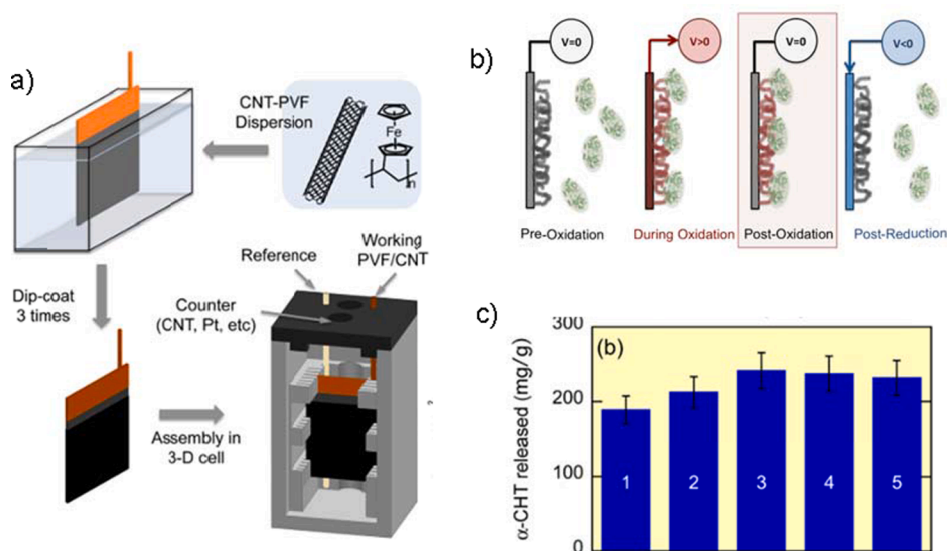
Using atomic force spectroscopy the interaction strength between

two interfaces can be determined directly, by following the deflection of a cantilever upon approaching a planar substrate. The cantilever can be equipped with a very sharp, conical, or colloidal probe, and the substrate can be an electrode (e.g. gold) in an electrochemical cell. As mentioned earlier this technique can be used to directly measure the double layer potential of an electrode [42,49,50] but also other surface forces [42]. Direct interactions between single molecules and interface can be measured by modifying the probes with macromolecules. The sample preparation and data interpretation are not trivial, however.

### 4. Conclusion

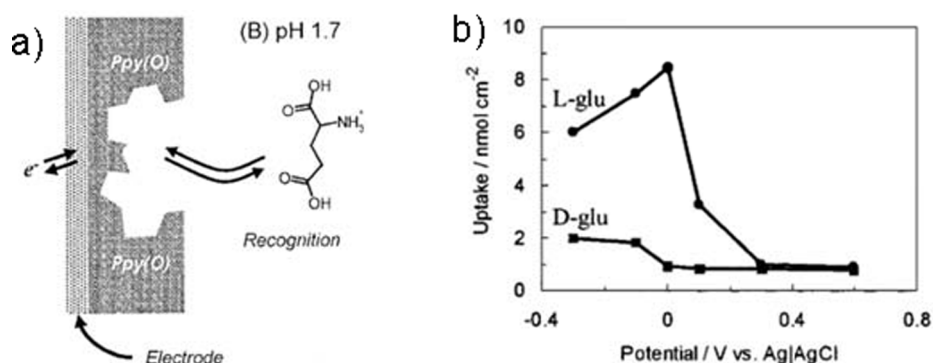
We summarized different approaches to use capacitive and faradic currents for the separation of ions as well as larger molecules such as proteins and even whole cells. Furthermore we discussed different electrode materials ranging from porous carbon to metallic surfaces and (electro responsive) coatings, such as conductive polymers or organo-metallics, for this purpose.

The overview and perspective that this review offers is important to position electrochemical separation processes that show a great potential as a next generation technology that answers today's challenges,



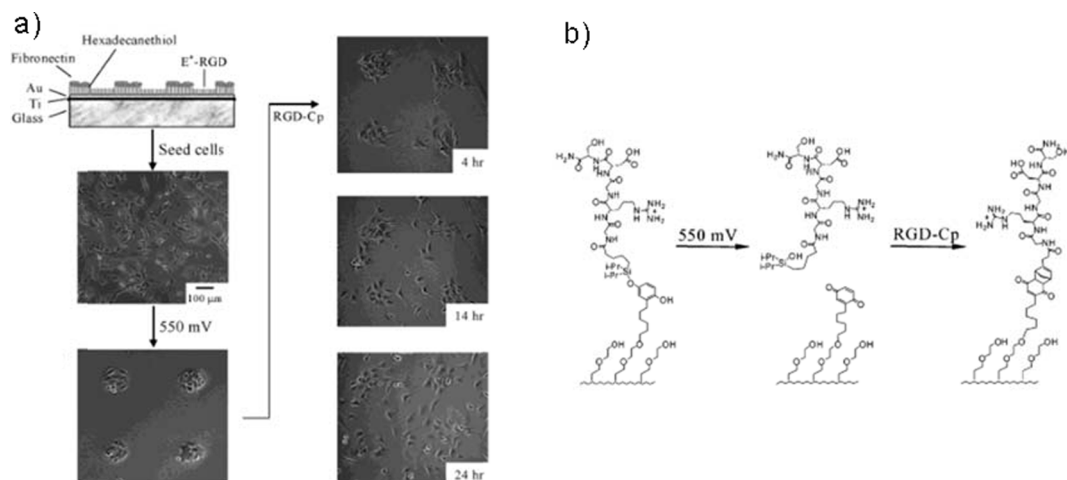
**Fig. 9.** a) Preparation of polyvinyl(ferrocene)/carbon-nano tube electrodes. b) Schematic of protein ad- and desorption depending on applied potential. c) Release of α-chymotrypsin.

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**Fig. 10.** a) Schematic of uptake/release of glutamic acid cation upon charging and discharging molecularly imprinted over-oxidized polypyrrole film at pH 1.7. b) Effect of applied potential on the uptake of 10 mM L- and D-glutamic acid.

Reproduced with permission from [182]



**Fig. 11.** a) Capture and release of fibroblast cells using a ligand that can be sacrificed when applying a potential of 550 mV to a hydroquinone-linker. b) Reaction scheme for the electro-responsive surface coating.

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**Table 4**

Overview of advantages and challenges of different methods to study the impact of an applied potential on ad- and desorption of macromolecules (e.g. proteins).

Techniques	Advantages	Challenges
E-Reflectometry	- Direct observation of changes at the interface	- Limited choice of substrates and therefore coatings - Influence of applied potential on measurement signal - Refractive indices need to be known - Difficult to distinguish nature of adsorbed species
E-SPR	- Direct observation of changes at the interface - Simple to use - High sensitivity	- Limited choice of substrates and therefore coatings - Influence of applied potential on measurement signal - Difficult to distinguish nature of adsorbed species
Assay/ UV detection in outlet/ Fluorescence in outlet	- Determine the change in concentration of specific species	- Sensitivity - No information about location of protein - Sampling, impurities
E-AFM	- Information about protein specific surface interactions - Quantification of interaction force	- Single molecule interaction - Difficult to operate and interpret - Limited choice of electrodes

such as improved and milder separations at reduced environmental impact. Therefore, we pointed out achievements and challenges for various species and indicated where cross-overs between the applications exist.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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