Electrochemical Nanoarchitectonics and Layer-by-Layer

Assembly: from basics to future

Gaulthier Rydzek^{a,b*}, Qingmin Ji^a, Mao Li^c, Pierre Schaaf^{d,e,f,g}, Jonathan P. Hill^{a,h},

Fouzia Boulmedais^{d,i}, Katsuhiko Ariga^{a,h*}

^a World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

^b International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

^c State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China.

^d Institut Charles Sadron, Centre National de la Recherche Scientifique, Université de Strasbourg, 23 rue du Loess, 67034, Strasbourg Cedex 2, France

^e Institut National de la Santé et de la Recherche Médicale, UMR-S 1121, "Biomatériaux et Bioingénierie", 11 rue Humann, 67085 Strasbourg Cedex, France.

^f Université de Strasbourg, Faculté de Chirurgie Dentaire, 1 place de l'Hôpital, 67000, Strasbourg, France.

^g Institut Universitaire de France, 103, boulevard Saint-Michel 75005 Paris, France.

^h Core Research for Evolutionary Science and Technology (CREST), Japan Science and Technology Agency (JST), 1-1 Namiki, Tsukuba 305-0044 Japan

ⁱ University of Strasbourg Institute of Advanced Study 5 allée du Général Rouvillois, 67083 Strasbourg, France.

Corresponding Authors:

RYDZEK.Gaulthier@nims.go.jp

1-1 Namiki, Tsukuba, Ibaraki, 305-0044 Japan

Phone/Fax +81-29-860-4832

ARIGA.Katsuhiko@nims.go.jp

1-1 Namiki, Tsukuba, Ibaraki, 305-0044 Japan

Phone/Fax +81-29-860-4832

Gauthier Rydzek was introduced to research in 2008 at the University of Montreal (master study). He earned his Ph.D. in physical chemistry from the University of Strasbourg in 2012 under the supervision of Fouzia Boulmedais, Jean-Claude Voegel and Pierre Schaaf. Joining Prof. Ariga's group at NIMS in 2013, he started working on electroclick chemistry coupled with electropolymerization as a postdoctoral JSPS Fellow. He recently became a fellow of the International Center for Young Scientists (ICYS), MANA, and devotes his current research to polymer-hybrids nanomaterials and catalysis.

Qingmin Ji earned her Ph.D. (2005) in chemistry from the University of Tsukuba. She started working as a postdoctoral fellow in National Institute for Materials Science (NIMS) from 2006 and became MANA scientist at World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA) in 2011. Her research currently focuses on the formation of layer-by-layer films and the application of mesoporous structures for delivery systems.

Prof. Mao Li received his Ph.D. degree from the Jilin University, China in 2007. He is

currently the group leader of Organic/Inorganic Nanomaterials Group at the Changchun Institute of Applied Chemistry (CIAC), Chinese Academy of Sciences (CAS). His research field is based on the electrochemical fabrication methodology for electronic devices and bio-relative applications.

Prof. Pierre Schaaf received an engineering degree from ESPCI (Paris) in 1982 and a PhD in Physical Chemistry from the University of Strasbourg in 1986. He spent most of his research career at the Institut Charles Sadron (ICS, CNRS) at Strasbourg and was appointed full professor in 1991 at the chemistry engineering school of Strasbourg (ECPM). Recently, he became a member of the Institut Universitaire de France (IUF) and was appointed director of INSERM unit 1121 “biomaterials and bio-engineering” in Strasbourg. His current research interests include polyelectrolyte multilayers and stimuli-responsive and bioactive films.

Jonathan P. Hill received his Ph.D. degree from Brunel University, U.K. in 1995. He is currently subgroup leader of the Supramolecules Group at the National Institute for Materials Science. Current research interests include synthesis and properties of tetrapyrroles and their supramolecular manifolds as well as unusual methods for preparing organic nanomaterials.

Fouzia Boulmedais received her PhD in physical chemistry from University Louis Pasteur in Strasbourg (France) in 2003. Her postdoctoral research at ETH-Z in Zürich (Switzerland) and MPI in Gölm (Germany) focused on the electrochemical response of multilayers of polyelectrolytes. She joined the Institut Charles Sadron in Strasbourg (France) where she got a position as CNRS researcher in 2006. Her current research involves polyelectrolyte films: their application in tissue engineering and their buildup by an electrical stimulus.

Prof. Katsuhiko Ariga received Ph.D. degree from the Tokyo Institute of Technology, Japan. He is currently the director of Supermolecules Group and Principal Investigator of World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA) at the National Institute for Materials Science (NIMS). His research field is based on supramolecular chemistry and surface science, including the boundary research areas of organic chemistry, physical chemistry, biochemistry, and materials chemistry. His major interests are the fabrication of novel functional nanostructures based on molecular recognition and self-assembly including Langmuir–Blodgett films, layer-by-layer films, and mesoporous materials.

KEYWORDS: Polyelectrolyte, water splitting, electroclick, supercapacitor, actuator, carbazole chemistry, corrosion

ABREVIATIONS

ABTS, 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate); AFP, α -1-fetoprotein; CEA, carcinoembryonic antigen; DTPA, dithiol phosphoramidite; EACC, 6-*O*-Ethoxytrimethylammoniochitosan chloride; EAP, electro-active polymer; ECC-LbL, electrochemical layer-by-layer; EDLC, Electrical double layer capacitor; FITC, Fluorescein isothiocyanate; FRET, Fluorescence resonance energy transfer; GO, graphene oxide; GOx, glucose oxidase; HA, hyaluronic acid; LbL, layer-by-layer; LPEI, linear poly(ethyleneimine); MEMS, microelectromechanical systems; MEPE, metallosupramolecular coordination polyelectrolytes; MNS, metal-oxide nanosheet; MWNT, multiwalled carbon nanotube; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; PAA, polyacrylic acid; PAA-C $\equiv$ CH, alkynated PAA; PAA-N₃, azidated PAA; PAH, poly(allylamine hydrochloride); PAH-Os, poly(allylamine hydrochloride) with osmium moieties; PAH-Fc, poly(allylamine hydrochloride) with ferrocene moieties; PAMPS, poly(2-acrylamido-methane-2-propanesulfonic acid); PANI, polyaniline; PB, Prussian blue; PEDOT, poly(3,4-ethylenedioxythiophene); PEI, poly(ethyleneimine); PEI-Fc, poly(ethyleneimine) with ferrocene moieties; PEM,

polyelectrolyte multilayer; PGA, polyglutamic acid; PLL, poly(L-lysine); PolyDADMAC, poly(diallyldimethyl ammonium); POM, poly(oxometalate); POSS, polyhedral oligomeric silsesquioxane; PSDAS, polystyrene-based diazonium salt; PV, polyviologen; PVP+, poly-1-methyl-2-vinylpyridinium; PVPOsBp, poly[(vinylpyridine)Os(bipyridyl)₂Cl^{2+/3}]; PXV, poly(hexylviologen); QCM, quartz crystal microbalance; RGO, reduced graphene oxide; SAM, self-assembled monolayer; SECM, scanning electrochemical microscopy; SEEC, simultaneous electropolymerization and electroclick; SPANI, sulfonated polyaniline; SrGO, sulfonated reduced graphene oxide; SPEEK, sulfonated poly(ether ether ketone); SWNT, single-wall carbon nanotube; TBTA, tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine; UME, ultra micro-electrode;

ABSTRACT

During the last few decades, electrochemistry and electrode modification have seen a tremendous fall off in creativity with the emergence of the nanoarchitectonic-based layer-by-layer (LbL) film deposition technique. An unprecedented variety of building blocks can be immobilized on surfaces, leading to progress in several fields including sensing, electrochromic, electro-responsive and energy devices. This review describes the state of the art of electrochemical devices based on LbL assemblies, with a focus on

supercapacitors, biosensors, and electroresponsive LbL such as electrodisolution/electroswelling of coatings. Recently, electrochemistry has also been used as an “active trigger” to induce the formation of films by covalent coupling, leading to new nanoarchitectonic approaches beyond the LbL strategy. These emerging electro-coupling reactions, including electroclick and carbazole chemistry, open new perspectives toward architecture and patterning of functional films and are extensively reviewed.

Graphical abstract:

Introduction

Nanotechnology promises exponential improvements in numerous fields including medicine, materials and energy devices. To date, our everyday life can already benefit from it through electronic devices. However, there have been relatively few practical applications in other fields. [1–3] Rising of nanodevices necessitates indeed a new concept to architect individual nanotechnologies into usable equipments: ordering building blocks at the molecular and macromolecular levels to achieve specific functions and cooperative properties. This concept, named "nanoarchitectonics", was introduced by Aono in 2000.[4–8] The application of nanoarchitectonics in nanomaterials,[9–11] biological interfaces,[12–18] and other applications[19–22] has been reported. At the same period, the layer-by-layer (LbL) assembly of films, membranes and capsules has undergone tremendous development, allowing the incorporation of an unprecedented range of functional building blocks into macromolecular platforms.[23,24] This approach can be integrated into the nanoarchitectonic concept, leading to versatile layered 2D materials. As recently reviewed, the LbL strategy is versatile toward the film deposition method,[25] the type of interaction between its building blocks,[26,27] and the resulting functional materials obtained.[28] However, no recent review has been released for highlighting the benefits

of coupling the LbL technique with electrochemical methods to achieve synthesis of nano-engineered devices. For instance, when deposited on electrodes, LbL platforms enable the design of a large variety of sensors, electro-responsive and energy-related materials. The first part of this review will focus on electro-active LbL films and their applications in electrochromism, electro-dissolution, sensors and supercapacitors. Electrochemical stimuli have also been recently used directly as a building trigger, leading to the development of various electrocoupling strategies including electroclick. Elaboration of advanced nanoarchitectonic films beyond the LbL method became thus possible, as reviewed in the second part of this paper. Therefore, LbL nanoarchitectonics under electrochemical control appears to be a key process towards the design of practical devices for use in our everyday lives.

1- LbL films and electrochemistry: an update

Perspectives opened by electrochemistry in the field of layer-by-layer (LbL) assemblies are extremely diverse and range from a fundamental understanding of electronic and ionic transfer to the design of applied devices. The first part of this review paper will be devoted to fundamental electrochemical mechanisms in LbL films, electro-responsive multilayers, and LbL-based devices for energy. A special emphasis has been placed on emerging applications.

1.1 - History and basic principles of polyelectrolyte multilayers

1.1.1 Two types of polyelectrolyte multilayers

The LbL technique involves the sequential deposition on a substrate of two species that interact spontaneously. The most common type of LbL assembly is based on alternating deposition of polyanions and polycations leading to polyelectrolyte multilayers (PEM).

When two strong polyelectrolytes are mixed in solution, stoichiometric polyanion/polycation complexes are formed with similar numbers of positively and negatively charged moieties.[29] According to this result, the alternating deposition of polyelectrolytes on a substrate should not result in formation of a multilayer film.[30]

Despite this fact, as first described by Decher, Hong and Schmitt in 1992, a regular film buildup could actually be observed when polyanions and polycations were sequentially deposited onto a substrate [31]. This was attributed to the presence of a surface-charge excess and its reversal after each deposition step.[32] [33] The excess charge originates from the polymeric nature of the polyelectrolytes and occurs for entropic reasons.

Indeed, an exact surface charge compensation would lead to a smaller number of chain configurations than a surface charge overcompensation, which allows formation of polymer loops extending into the solution. The first reported LbL multilayer film was composed of poly(styrene sulfonate) (PSS) as polyanion and poly(allylamine

hydrochloride) (PAH) as polycation.[23] Film thickness increased linearly with the number of deposition steps, presenting a stratified structure. Under the buildup conditions used, each layer in the film was only able to interact with the 3 to 4 neighboring layers. This stratified structure allowed a fine tuning of the film structure and composition and incorporation of active species at precise locations could thus be achieved. These films were denoted as "linearly growing films". Von Klitzing and Möhwald demonstrated that the diffusion coefficient of Rhodamine in linearly growing PSS/PAH multilayers was as low as $10^{-15} \text{ cm}^2/\text{s}$.[34] The polyelectrolytes multilayer appeared thus essentially frozen in the stratified LbL film. Until 1999, it was accepted by the scientific community that the thicknesses of polyelectrolyte multilayers always increase linearly according to the number of deposition steps. However, by investigating the buildup of poly(lysine) and alginate, Hubbell and coworker found a film whose thickness increased exponentially.[35] Picart *et al.* confirmed this result using the hyaluronic acid/poly-(L-lysine) (HA/PLL) system.[36] Exponential growth of films is related to the ability of one or both of the polyelectrolytes to diffuse in and out of the film during each bilayer deposition step. A schematic representation of the exponential film growth mechanism is presented in figure 1.[37,38]

Figure 1: Exponential growth mechanism.[37,38] Diffusion of at least one polyelectrolyte (the polycation in this scheme) within the film allows accumulation of an increasing amount of reactant, leading to larger mass increments at each deposition step.

In contrast to films grown in the linear regime, exponentially grown ones are poorly structured and behave as very viscous liquids. For instance, the diffusion coefficient of PLL chains in an exponentially growing HA /PLL multilayer is close to $10^{-8} - 10^{-9} \text{ cm}^2/\text{s}$, which is 6 - 7 orders of magnitude faster than the diffusion of PSS in linearly growing PSS/PAH films.[39] Polyelectrolytes diffusing into exponential films can also exchange with polyelectrolytes of the same charge present within the multilayer. Fluorescent

PLL^{FITC} could exchange with unlabeled PLL in an HA/PLL film.[37] Even more strikingly, PAH could also replace PLL in a similar film.[40] Exponential film growth appears to be favored by weak interactions between polyelectrolytes, whereas strong interactions favor linear growth of coatings. In an attempt to quantify this, Laugel *et al.* demonstrated that linear growth is observed when polyanion/polycation interactions in solution are exothermic while exponential growth occurs when interactions are endothermic.[41] This observation suggests that spontaneous polyanion/polycation complex formation is driven by a decrease of the Gibbs free energy, ΔG . ΔG has two contributions: a negative entropic contribution partly due to the release of counterions around the polyelectrolytes during the complex formation,[29] and an enthalpic contribution. The enthalpic contribution depends on coulombic charge interactions (between polyelectrolytes, between polyelectrolytes and counterions and between the counterions themselves) and water restructuration, and can be positive (endothermic) or negative (exothermic). When it is exothermic the enthalpic contribution reinforces the entropic effect and the polyanion/polycation interactions are strong. The film should then form dense structures, preventing diffusion of polyelectrolyte chains and leading to a linear growth. When the enthalpy term is positive (endothermic process), complexation is entirely entropically driven. Interactions between polyanions and

polycations are then much weaker and the film are less dense, allowing polyelectrolyte diffusion and exponential film growth. Because the nature of the ions and their concentrations affect both the enthalpic and the entropic term of ΔG , these parameters also affect the growth process. Indeed, PSS/PolyDADMAC (PolyDADMAC: poly(diallyldimethyl ammonium)) undergoes linear growth in the absence of added salt to the polyelectrolyte solutions but exponential growth when the salt concentration is increased. For a given salt concentration, kosmotropic anions (increasing the stability of intermolecular forces) favor a linear growth and chaotropic anions (decreasing the stability of intermolecular forces) favor exponential growth.[42]

1.1.2 Internal charges and the Donnan potential

Polyelectrolyte multilayers result from complex interactions between polyanions, polycations and counter-ions. Exact charge compensation between polyanions and polycations can occur, although this is not a strict requirement. Moreover, even if charges of polyanions and polycations are exactly balanced, they may not neutralize each other locally; counterions can thus locally neutralize charges. Schlenoff introduced the concept of intrinsic and extrinsic charge compensation, which is schematically depicted in figure 2.[43]

Figure 2: Intrinsic and extrinsic charge compensation. [43] Charge neutralization occurs directly between polyelectrolyte chains (intrinsic process) or by inclusion of counterions in the LbL film (extrinsic process).

Intrinsic charge compensation corresponds to direct compensation between polyanions and polycations, while in contrast extrinsic charge compensation is due to local charge neutralization involving counterions. Extrinsic charge compensation must occur if there is an excess of one polyelectrolyte in the film although it can also be present when there is exact charge compensation between polyanion and polycation charges. The film then contains additional anions and cations whose total charges are equal. When one polyelectrolyte is in excess, the multilayer acts as an ion semi-permeable membrane with an excess of “fixed” charges to be neutralized. This induces an electric potential difference between the film and the contacting solution called the **Donnan potential**. This potential tends to confinement of oppositely charged counterions in films containing an excess of "fixed charges" for restoring its electrical neutrality, and rejects same-charged counterions (semi-permeable membranes).[44,45] The Donnan potential

also exists even when no fixed charges are present in the film, as in the case of exact intrinsic charge compensation. This is due to excess charge present at the outer layer of the coating (i.e., the charge overcompensation remaining after each deposition step). The potential due to the charge excess at the outer layer decreases exponentially into the film, leading to a pH change inside the multilayer, and was observed in 1995 in a PSS/PAH film.[46] A direct measurement of the surface-charge excess induced Donnan potential was achieved by Calvo and Wolosiuk in 2002.[47]

This simple situation raises a fundamental question which is still under debate: is there exact charge compensation between polyanions and polycations in a multilayer LbL film. In fact, both exact and non-exact charge compensation situations can be found. As early as 1996 Hoogeveen *et al.* found a stoichiometric factor f (ratio between the number of cationic and anionic charges of polyelectrolytes in a multilayer) of the order of 3 for poly-1-methyl-2-vinylpyridinium (PVP⁺)/PSS multilayers.[48] At intermediate NaCl concentrations ($0.1\text{M} < [\text{NaCl}] < 0.75\text{ M}$) the PSS/PolyDADMAC film also presents an excess of PolyDADMAC chains.[49] Using radiolabelling techniques, Schlenoff's group found that for small numbers of PSS/PolyDADMAC bilayers, there is exact compensation between PSS and PolyDADMAC charges[43] whereas for larger

numbers of bilayers (typically exceeding 12-18) exact intrinsic charge compensation no longer exists in PSS/PolyDADMAC multilayers.[50] Another method to investigate this question involves using the Donnan potential that appears in electrochemical reactions taking place at a multilayer/electrode interface. Anson showed that the Donnan potential between a polyelectrolyte film deposited on an electrode and the contacting electrolyte solution contributes to the formal potential measured for redox couples incorporated in the polyelectrolyte coating.[51,52] For example, El Haitami *et al.* showed that the apparent redox potential of ferrocyanide ($\text{Fe}(\text{CN})_6^{4-}$) ions in a PSS/PAH multilayer film depends upon the kind of salt used for the buildup.[53] This variation is due to the Donnan potential in the film, indicating an extrinsic charge imbalance in PSS/PAH multilayers. Positive Donnan potentials ranged from + 50 mV for film buildup with F^- anions to + 90 mV with ClO_4^- ions. Indeed, chaotropic ions interact more strongly with PAH than kosmotropic ones. As a result, chaotropic ions such as ClO_4^- partially neutralize the positive charges of the PAH chains during buildup and the remaining positive charges are neutralized by the negative charges of PSS. However, these ClO_4^- ions are not fixed and they can thus be considered as extrinsic charges. There is a resulting imbalance between positive and negative fixed charges in the film with an excess of fixed positive charges. Such a phenomenon should be rather general, leading

to a Donnan potential inside the films and a resulting exclusion of ions of the same charge as the fixed charges within the film. For instance, cyclic voltametry measurements with ruthenium(III) hexaamine ($\text{Ru}(\text{NH}_3)_6^{3+}$) lead to no current, in contrast to ferrocyanide ions, confirming the presence of excess "fixed" positive charges within the PSS/PAH film. [53] However, these probes lead to similar currents with PSS/PolyDADMAC films having less than 10 bilayers, proving that both species could penetrate to the film, replacing either Cl^- or Na^+ ions, and suggesting the absence of Donnan potential.[54] This confirmed the almost exact charge compensation in PSS/PolyDADMAC films.

The next question to be answered concerns the presence of counterions other than those compensating the charge excess. By using radiolabelling techniques, Schlenoff revealed the virtual absence of counter-ions in intrinsically compensated PSS/PolyDADMAC multilayers for small numbers (up to 10) of bilayers.[43] Subsequently, Durstock and Rubner came to the conclusion that PSS/PAH films assembled without salt contain around 1 small ion per 10000 repeat units by considering conductivity and dielectric measurements.[55] The number of small ions can increase to at least 1 small ion per 1000 repeat units for films constructed in the presence of salt. However, these experiments did not establish the nature of the counterions. Indeed, by performing

conductivity experiments on PSS/PAH multilayers build with different alkali ions, Schönhoff *et al.* found that the PEM conductivity does not depend on the nature of the alkali ion.[56] Because these ions diffuse within the polyelectrolyte complexes their concentration must be extremely small. This conclusion is not unexpected if one refers to the findings of El Haitami *et al.* who found an excess of fixed positive charges in a PSS/PAH multilayer.[53] As far as the anions (Cl⁻ in their case) are concerned, no conclusion can be drawn because it seems that in these polyelectrolyte complexes Cl⁻ ions do not contribute to ionic conductivity.[57] Hydrophobic properties of polyelectrolytes are suggested to be responsible for the small concentrations of ions in PEMs.[58]

1.1.3 Ionic conductivity in polyelectrolyte multilayers

In any material, ionic conductivity is given by the relationship:

$$\sigma = \sum_i \rho_i z_i \mu_i$$

where the sum involves all the ionic species, ρ_i represents the number density of ions of type i , z_i represents their charge and μ_i their mobility. By using impedance and dielectric measurements, Durstock and Rubner found very low conductivities increasing from 1×10^{-12} S/cm for poly(acrylic acid) PAA/PAH films in the dry state to 2×10^{-7}

S/cm in the presence of water. [55] For this system the conductivity depended on the multilayer buildup conditions (pH and ionic strength of the polyelectrolyte solutions). For PSS/PAH multilayers, the conductivity was around 2×10^{-12} S/cm at 140 °C. These two examples demonstrate what appears to be a rather general result: the ionic conductivities of PEMs are usually low. Indeed, the polyelectrolytes do not contribute significantly to the ionic conductivity because their mobility μ_i is extremely low. Any conductivity should thus originate mostly from the small counterions present in the multilayer. However their concentrations are usually very low and they are also usually bound to the polyelectrolyte fixed charges. Ions move by hopping from trap to trap within such films with their diffusion coefficients depending on the salt concentration as $\bar{D} \approx k[\text{salt}]^n$ with n of the order of 3 to 4.[54,59] Due to these ion/polyelectrolyte interactions, the mobility of counterions is also strongly coupled to the polyelectrolyte dynamics: more highly mobile polymeric chains lead to higher ionic mobilities.[60] Variation of several parameters permits increases in ionic conductivity of PEMs including the use of weak polyelectrolytes such as PAA deposited under pH conditions where they are only partially charged. The local mobility of polyelectrolyte segments can also be increased by using polyelectrolytes that act as plasticizers. Finally, the interactions between small ions and fixed charges can be decreased when using large

ions with delocalized charge. Following these directions DeLongchamp and Hammond designed polyelectrolyte multilayers with conductivities that reached 10^{-5} S/cm, suitable for certain applications.[58] To achieve these conductivities they used linear poly(ethylene imine) (LPEI) as polycation, poly(2-acrylamido-2-methyl-1-propanesulfonate acid) as a hydrophilic, plasticizer polyanion, or partially charged PAA. They also used $(\text{LiCF}_3\text{SO}_3)$ as anion with delocalized charge. The group of Schönhoff performed systematic investigations of ionic conduction in PSS/ PolyDADMAC multilayers in the dry state and at various levels of hydration observing that ionic conductivity increased exponentially with the degree of hydration. [61] In hydrated states, the conductivity was dominated by protons. In the dry state, when using X^+Cl^- salts where X is an alkali metal cation, the conductivity was dominated by these cations even with an excess of polycation. [61] This behavior was explained as being due to a micro-phase separation in the film into neutral and charge-rich regions with no communication between the charged areas. The ion hopping process was thermally activated and conductivity increased with temperature. The conductivity measurements were correctly fitted by the Mismatch Generated Relaxation for the Accomodation and Transport of Ions model introduced by Funke.[62] This model considers microscopic ion hopping in an energy landscape

that changes with time. It should be of interest to compare this model to the ion hopping model introduced by the group of Schlenoff.[59]

1.2- Electro-responsive LbL films

Stimuli-responsive polymer materials, which adapt to the surrounding environment, have a wide range of potential applications including in 'smart' optical systems, micro-electromechanical systems and for drug delivery.[63] The following section of this review will focus on the different electro-responsive LbL films that have found application in these three domains.

1.2.1 Electrochromism of LbL films

An electrochromic material is able to reversibly change its color under an applied potential or an applied electric current usually involving some electrochemical reaction(s). Electrochromic films are currently attracting much interest in academia and industry, with applications including dynamic windows, panel displays and smart paper. Electrochromism is based on the reversible change of a molecule between two redox

states associated with distinguishable absorption or reflection spectra.[64] This change relies on the electronic states of the chemical species involved, especially the π or d-electron states. Recent advances in the field of electrochromic materials obtained by different processes have been described in several other reviews.[64–66] The active material in electrochromic LbL films is either a redox polymer or an inorganic nanoparticle. Thus, two main types of LbL films can be found: purely organic ones based on conjugated polymers, and hybrid ones based on conjugated polymers and inorganic nanoparticles. Most LbL electrochromic films are assembled by electrostatic interactions although a few studies have shown that they can be built upon coordinative interactions to obtain metallo-polymer networks. Two parameters can be used to compare electrochromic coatings: switching time, defined as the time required to reach 90% of full absorbance change, and the optical contrast defined as the maximum of absorbance change when a potential is applied.

Organic LbL films

π -conjugated polymers are of a great interest for the development of electrochromic devices. In this case, variation in color of the films was obtained by p-doping/dedoping processes upon oxidation/reduction of the polymer, accompanied by the transport of

electrons and ions. Several conjugated polymers have been used in LbL films for electrochromic applications including polythiophene derivatives,[67] polyaniline,[68,69] and viologen-[70–76] or triphenylamine-containing polymers.[70] In 1997, Schlenoff and co-workers used positively charged poly(viologen) (PV) and negatively charged poly(styrene sulfonate) (PSS) in the first study of the electrochromic properties of LbL films.[71,72] PV was fully electrochemically accessible within the film due to interpenetration of PV and PSS layers. Later, in 2001, a fully functional switchable electrochromic LbL based device was developed by Hammond and co-workers.[67] Two LbL films, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) colloid/linear poly(ethylene imine) (PEDOT:PSS/LPEI) and poly(2-acrylamido-methane-2-propanesulfonic acid)/poly(aniline) (PAMPS/PANI) were deposited on two ITO glass plates. PAMPS was used as an electrolyte gel between the two functionalized ITO electrodes while PEDOT and PANI based LbL films constituted cathodic and anodic colored films, respectively (figure 3). The resulting solid electrochromic device gave a maximum optical contrast of 30% within one second from a blue-green color to yellow. The optical contrast, from a light blue color to purple blue, was increased to 82% by replacing PANI with poly(hexylviologen).[77] This contrast remains one of the highest reported for purely polymer electrochromic devices. However,

increasing the number of layers increased the optical contrast but also led to longer switching time.[77] To avoid the use of PEDOT:PSS colloids, a negatively charged PEDOT was used in combination with PAH. The resulting films showed optimized electrochromic properties with respect to both switching time and optical contrast. The loss of efficiency for greater numbers of bilayers was attributed to an inability to access all sites in the thicker films.[78]

Figure 3: Electrochromic solid device based on LbL electrochromic film developed by DeLongchamp *et al.*[67] PEDOT and PANI are the electrochromic polyelectrolytes allowing the color switch of the device from a blue-green to a yellow color.

Electrochromic LbL films were also prepared by sequential electrostatic deposition of PSS and pre-formed metallosupramolecular coordination polyelectrolytes (MEPE). MEPE based on ditopic bis-terpyridine moieties coordinated to cobalt allowed tuning of the optical properties of the films with good long-term stabilities and an optical contrast of 16% with switching time of 1 s.[75] To avoid the use of non-electroactive polyelectrolytes that could obstruct ions/electrons transport and thus reduce both the

contrast and the response time, electrochromic LbL films were assembled using coordinative interactions (Figure 4). Assembled by sequential electrostatic deposition of PSS and pre-formed metallocupramolecular coordination polyelectrolytes based on ditopic bis-terpyridine moieties coordinated to cobalt, coordinative interaction based LbL films allowed tuning of the optical properties of the films with good long-term stabilities and an optical contrast of 16% with switching time of 1 s (Figure 4a). Later, Maier *et al.* used polyiminoarylene functionalized with terpyridine moieties and assembled by coordination through zinc hexafluorophosphate (ZnPF_6) in an organic solvent (Figure 4b). [79] The stable arylene units and easily oxidizable amine groups resulted in electrochromic properties while terpyridine substituent groups allowed coordinative self-assembly with metal ions. Oxidation of the coordination polymer films induced color changes from yellow to blue. The switching time, at an applied potential of 0.56 V, was about 0.45 s which is faster than the ones obtained for electrostatic electrochromic LbL films. A quasi-reversible change was obtained with different colors depending on the ions used, with an optical contrast of 18%. [79,80] This value is comparable to electrostatic LbL films with the same number of layers. [78] In order to obtain a double electrochromic film, zinc salts of the redox active dianion 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) or

poly-(4-sulfonatophenyl)iminofluorene were used instead of ZnPF_6 in the LbL assembly of polyiminoarylene-tpy.[81] Due to oxidation of the two chromophores present in LbL films, *i.e.* the polymer and the redox active zinc, higher contrasts were obtained.

Figure 4: Electrochromic films based on coordination interactions.[75,79] Electrochromic LbL films relying on (a) metallosupramolecular coordination polyelectrolytes alternated with a polyanion and (b) coordination interactions between polymer functionalized by terpyridine moieties and divalent ions.

Hybrid LbL films.

Hybrid organic-inorganic LbL films have synergetic properties combining the elasticity and the properties of organic polymers with the high thermal and chemical stability of inorganic compounds. Active inorganic nanoparticles, such as Prussian blue (PB),[82,83] poly(oxometalates) (POMs)[84–88] and tungsten oxide (WO_3)[89,90] have been used to

assemble electrochromic films. Hybrid LbL coatings can also incorporate inactive inorganic building blocks such as polyhedral oligomeric silsesquioxane (POSS)[68,91] and graphene.[83,92] Semiconducting oxides can undergo reversible electrochemical reduction–oxidation of the transition metal by insertion–deinsertion of positive ions and electrons into the oxide structure. PB is a negatively charged iron(III) hexacyanoferrate that can be switched from a colorless reduced state to a deep cyan oxidized state. When the number of deposited layers was increased, PB/PANI LbL films exhibited a switching time ranging from around 0.31 s to 1.62 s and a contrast ranging from 8.2% to 61.1%.[82,93] PB based LbL films are superior in terms of contrast compared to PB single films,[93] but, in the current smart windows device material, WO_3 exhibits higher coloration efficiency and better cycle stability compared with other transition metal oxides. When it is included in LbL films, it can be reversibly reduced from colorless or pale yellow to a blue color.[84,94] The first POM-based LbL films for electrochromism applications were assembled in 1998 by using poly(diallyldimethylammonium chloride) and sodium decatungstate nanoparticles.[84] POM-based films offer a reduced conductivity, which allows to maintain the film color without applying any current. An improvement of the electrochromic response of POM-containing LbL films are generally obtained by secondary doping of π -conjugated polymers but also by enhancement of the

electroactive properties of POMs.[88] Recently, the first example of an inorganic multicolored photoluminescence switching LbL film was developed by alternate deposition of POMs and CdSe@CdS core-shell quantum dots. The tunable FRET between quantum dots and the reduced state of POMs induced photoluminescence with a quick response (off 17 s, on 38 s), high on/off contrast (91%) and good cycling performance.[95] PANI based hybrid electrochromic devices were intensively studied. The color of reduced graphene oxide/PANI multilayer films changed from yellow to green due to PANI oxidation with an optical contrast comparable to PANI based electrochromic devices, but with a better electrochemical stability.[92] In the case of sulfonic acid-grafted reduced graphene oxide (S-rGO)/PANI LbL films, a much faster electrochromic switching kinetics was obtained compared to spin-coated PANI thin films.[96] Incorporation of graphene resulted in drastic improvements in electrical and ionic conductivities of LbL films, enhancing their switching time. Lu and co-workers developed copolymerized polyaniline-tethered, polyhedral oligomeric silsesquioxane (POSS-PANI) with a star-like molecular geometry. In solution, this system lead to a much higher electrochromic contrast than PANI, attributed to more accessible doping sites and facile ionic movement during redox switching.[97] When incorporated in LbL films with sulfonated polyaniline (SPANI), POSS-SPANI allowed to improve the switching kinetics

of the film compared to spin-coated SPANI.[69] Another type of inorganic NP has recently been reported: silsesquioxane groups could be combined with viologen in water-dispersed NPs and associated with PAMPS. A high contrast of about 50% could be achieved with a switching time in the solid state of 3 s.[91] Performances from the main electrochromic LbL systems are summarized in table1.

Table 1: performances of LbL electrochromic films.

Organic LbL films			
System	Contrast ratio (%)	Switch	Ref
PEDOT:PSS/LPEI	24.5% at 654 nm (20 bilayers)	< 2s	[67]
PAMPS/PANI	51.7% at 780 nm (20 bilayers)	< 2s	[67]
PEDOT:PSS/PXV	82.5% at 525 nm (45 bilayers)	3 s	[77]
PEDOT-S/PAH	45% at 530 nm (40 bilayers)	> 2.5 s	[78]
	20% (20 bilayers)	2.5 s	
	10% (10 bilayers)	2.5 s	
PSS/Co-MEPE	16% at 643 nm (40 bilayers)	1 s	[75]
poly(terpyridylphenyliminofluorene)/Zn acetate	18% at 375 nm (12 bilayers)	0.45 s	[79]
poly(terpyridylphenyliminofluorene)/Co acetate	8.5% at 375 nm (12 bilayers)	0.32 s	
poly(terpyridylphenyliminofluorene)/Ni acetate	5% at 375 nm (12 bilayers)	0.50 s	
poly(terpyridylphenyliminofluorene)/ZnPF ₆	18% at 800 nm (12 bilayers)	0.45 s	[81]
poly(terpyridylphenyliminofluorene)/Zn-ABTS	33% at 800 nm (12 bilayers)	0.38 s	
poly(terpyridylphenyliminofluorene)/Zn-poly(4-sul	27% at 800 nm (12 bilayers)	0.43 s	
fonatophenyliminofluorene)			
Poly(terpyridyl iminoarylenes) 3, 6/Zn	24.6% at 300 nm (12 bilayers)	0.3 s	[98]
Poly(terpyridyl iminoarylenes) 3, 6/Co	10.8% at 300 nm (12 bilayers)	1.1 s	
Poly(terpyridyl iminoarylenes) 3, 6/Ni	14.5% at 300 nm (12 bilayers)	0.4 s	
Hybrid LbL films			
System	Contrast ratio (%)	Switch	Ref
PB/PANI	61.1% at 750 nm (30 bilayers)	1.62 s	[82]
	26.4% at 750 nm (15 bilayers)	0.90 s	

	15.4% at 750 nm (10 bilayers)	0.66 s	
Graphene/PANI	12% at 700 nm (15 bilayers)	6 s	[92]
SrGO/PANI	30% at 700 nm (25 bilayers)	6 s	[96]
POSS-PANI/SPANI	26% at 592 nm (50 bilayers)	60 s	[69]
POSS-PANI/PAMPS	19% at 626 nm (50 bilayers)		
PXV NPs/PAMPS	50% at 633 nm (40 bilayers)	3 s	[91]

PV polyviologen, PXV : poly(hexylviologen), PEDOT-S: Poly(4-(2,3-dihydrothieno [3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butanefulfonic acid, sodium salt), ABTS: 2,2'-azino-bis(3-ethylbenzo-thiazoline-6-sulfonate), SPANI: sulfonated polyaniline

1.2.2 Electro-swelling of LbL films

Microelectromechanical systems (MEMS) generally incorporate at least one type of transducer that converts electrical energy to mechanical energy. Electroactive polymers (EAPs), also referred to as artificial muscles, are an emerging transducer technology which is low in cost, compatible with a variety of fabrication techniques and able to withstand a wide range of environmental conditions. EAPs might find applications in several fields, including robotics, automation, prosthetics, artificial organs, etc.[99] Due to their fast switching times (less than 1 s) and low voltage thresholds (less than 1 V), electroresponsive LbL films represent ideal systems as artificial muscles or actuators. Electroresponsive LbL films are also promising platforms for the *in situ* study of cell response to the mechanical properties of the substrate. Electro-swelling/deswelling of LbL films have been mostly developed by incorporating redox active molecules inside

the film. Oxidation or reduction of redox active species induces a change of their electrostatic charge with an electron transfer to or from the electrode. To maintain its electroneutrality, the LbL film undergoes a swelling/deswelling due to exchange of ions and solvent with the external electrolyte. Redox active molecules can be incorporated in an LbL film using three different methods: (i) by grafting the molecule onto one of the two polyelectrolytes used to build the film,[47,100–103] (ii) by incorporation after the film buildup [104–106] or (iii) by its incorporation as one component of the film[107,108] (Figure 5).

Grafting of electro-active molecules on the polyelectrolytes. The first contribution in the field of electro-responsive LbL films came from Calvo's group in 2002 using polyelectrolytes functionalized with redox-active moieties (Figure 5a). The swelling/deswelling phenomenon under electrochemical stimulus was described for LbL systems based on PAH functionalized with osmium complex (PAH-Os).[47,100–102] Glucose oxidase (GOx)/PAH-Os LbL film was subjected to oxidation/reduction cycles inducing the swelling/deswelling of the film.[101,102] The same phenomena was found in PSS/PAH-Os, poly(vinyl sulfone)/PAH-Os and GOx/PAH-Fc LbL films. It was attributed to the incorporation or exclusion of counterions and/or water molecules from

the electrolytic solution.[47,103,109]

Figure 5: Electro-swelling processes of LbL films. Electro-swelling/deswelling of LbL films based on (a) redox active moieties grafted onto one of the polyelectrolytes, (b) free redox active molecules confined in LbL film and (c) redox active component based film

Confinement of electro-active molecules after film buildup. Free electro-active molecules can be incorporated into exponentially grown films leading to electroresponsive properties in those films.[104–106,110,111] Under an applied potential, oxidation of ferrocyanide ions confined in a polyglutamic acid (PGA)/PAH LbL film, leads to a loss of

one charge per molecule. To compensate for this loss of charge, counteranions diffuse into the LbL film with their hydration shells, consisting of several water molecules, inducing a swelling of the film (Figure 5b). The reversibility of the oxidation/reduction process of ferrocyanide ions leads to a consequent reversibility of the swelling/deswelling of the film. The swelling could be tuned by using different types and concentrations of salts present in the supernatant solution in contact with the electroresponsive films.[47,103,106] Higher concentrations of salt or kosmotropic monovalent ions leads to increased uptake of water (hydration) of LbL films and thus to a higher swelling ratio.[106]

Incorporation of electro-active molecules as one component of the film. The incorporation of cations by polyviologen based LbL films subjected to cyclic voltammetry was first studied by Schlenoff.[43,73] Later, Prussian blue (PB) containing coatings were widely studied. LbL films containing redox active components such as PB[107] or electropolymerized polypyrrole[108] underwent a reversible swelling when subjected to an electric potential (Figure 5c). Variations in the thicknesses of the electroresponsive LbL films were in general between 5 and 25%, depending on the system but also on the ions present in solution.[105–107,112] Furthermore, their Young's

elastic moduli also varied with the change in film thickness. Upon reduction, PB/LPEI LbL films exhibited a reversible decrease in their Young's modulus from 3.40 to 1.75 GPa. PAA/poly(benzyl viologen) LbL films underwent a reversible change of their Young's moduli from 10 MPa to 75 MPa when the reduction potential of benzyl viologen was applied.[113] Also, the stiffness of DNA /PEI-Fc LbL films could be tuned between ~2 and 0.5 MPa by applying an electrochemical stimulus and depending on the oxidation rate of Fc groups. This tunable stiffness allowed control over the adhesion of fibroblast cells to the film from being an extended spread-out shape to a round shape depending on the applied potential.[112] However, the inclusion of redox active species in LbL films is not a strict requirement for obtaining electroswelling/deswelling activity. Indeed, Hammond and co-workers showed that pH changes caused by water electrolysis could induce this phenomenon on PSS/PAH LbL films with a concurrent change of the Young's Modulus.[114]

1.2.3 Electro-dissolution of LbL films

Controlled drug release systems are usually designed for the sustained release and maintenance of drug levels over lengthy periods of time within a narrow concentration range in order to avoid toxicity at excessive concentrations and ineffectivity at low levels

of the drug. However, most of the available systems give a gradual reduction in drug release rate rather than any actual control. There is also an increasing interest in developing drug release systems than can be triggered directly by a change in its local environment or by some stimulus applied by an operator. Surface mediated drug delivery has several biomedical applications, such as in drug eluting stents, delivery of antibiotic or anti-inflammatory drugs, transcutaneous delivery of vaccines, etc...[115] Control of the timing, duration and dosage of drug release might be available by using an applied stimulus such as an electrochemical signal. Thus, the property of some LbL films to be dissolved under an applied current or voltage[116,117] has been used to develop different platforms for the release of model molecules[118–121] or bioactive molecules, such as polysaccharides,[122–124] plasmid DNA[125–127] and antibiotics[128] but also for cell sheet engineering.[129,130] Electrodissolution of LbL films relies on a weakening of the interactions between its components. This can be obtained by direct redox reaction of the film constituents or by changing a property of the local environment such as the pH, for instance, by water electrolysis.

Figure 6: Electro-dissolution processes of LbL films. Electrodissolution of LbL films obtained from (a) PB/LPEI LbL where PB loses its ionization under an oxidative potential,[93] (b) heparin/PLL LbL where the electrolysis of water induces counterion diffusion and a decrease in pH [122] and (c) DNA/ Zr^{4+} where reduction of Zr^{4+} disturbs the assembly which is based on electrostatic and coordination interactions between Zr^{4+} ions and phosphate groups of DNA. [125,131]

Direct redox reaction of the film constituents. The first study on the electrodisolution of LbL films was made by Hammond and co-workers using PB/LPEI films. Electrostatic interactions between nanoparticles and LPEI were removed due to the loss of ionization of PB by its oxidation by applying a potential of 1.5 V (vs SCE, *i.e.* 1.9 vs Ag/AgCl) (Figure 6a).[93] Using this property, Wood *et al.* succeeded in controlling the release of dextran sulfate from PB/LPEI coatings.[123] Later, incorporation of electroactive

polyelectrolytes[120,121,124,132] or ions[125,131] in LbL films allowed variation of the electrostatic charges in LbL films and disruption of their integrity. It is also possible to work at the redox potential of the electroactive moieties. Wang *et al.* studied the buildup and electrodisolution of DNA/Zr⁴⁺ LbL films based on electrostatic and coordination interactions between Zr⁴⁺ and phosphate groups of DNA. These LbL films could be dissolved by reduction of Zr⁴⁺ with the application of a mild electric potential (-0.6 V vs Ag/AgCl) (Figure 6c). Release of DNA was demonstrated, thus allowing cell transfection.[125,131]

Local modification of the environment. Dissolution of non-electroactive LbL films was first reported by Boulmedais *et al.* by using the electrolysis of water (oxidation), obtained above 1.8 V (vs Ag/AgCl) (Figure 4b).[122] Controlled release of heparin from heparin-based LbL films could be obtained by turning the applied potential on and off. A combination of two effects could explain the dissolution of LbL films: pH changes at the surface of the electrode due to water electrolysis, and ion migration into the film.[116,122] When DNA/PLL films were used, a faster dissolution with a consequent faster release of DNA was observed at 1.8 V if the film was constructed under an applied potential of 1.2 V (vs Ag/AgCl).[126] (Figure 6b) In that case, the dissolution was related

to pH change but also to local formation of HClO, which reacted with amino groups of PLL thus altering their electrostatic charge. Several systems have been developed to achieve electrodissoolution at lower electrical potential. Based on specific interactions, avidin and 2-iminobiotin-labeled PEI LbL films decomposed under an applied potential of 0.6–1.0 V (*vs* Ag/AgCl) by changing the environmental pH from basic to weakly acidic.[133] Dissolution of hydrogen-bonded thin films could also be obtained at -0.56 V (*vs* Ag/AgCl). By using an hydrolytically degradable poly(β -amino ester) as polycation, Lynn and co-workers obtained a fast release of intact plasmid at -1.1 V (*vs* Ag/AgCl).[127] Release of molecules could also be obtained without LbL electrodissoolution. For instance, when an electrical potential just strong enough for commencement of water electrolysis was applied (oxidation at 1.2 to 1.5 V, *vs* Ag/AgCl), local acidification lead to weakened interactions between the released molecule and the PAA/PAH film without dissolving it.[118] Vörös and co-workers developed an elegant platform based on LbL films containing embedded liposomes for the release of a model drug by applying an electrochemical stimulus.[134,135] Changes of local pH and ionic strength probably increased the permeability of liposomes membrane. Calcein could be successfully released inside living cells by application of a 50 $\mu\text{A}/\text{cm}^2$ stimulus.

Spontaneous electrochemical processes: the case of anticorrosion coatings.

Electrochemical corrosion processes imply local pH modifications that can be used as a trigger for releasing anticorrosion inhibitors. The group of Shchukin has extensively studied various immobilization strategies of inhibitors inside anti-corrosion coatings.[136–140] For instance, the LbL technic can be employed for assembling inhibitor-loaded nanocontainers that are pH-sensitive and can be dispersed into polymer coatings. When corrosion of aluminum or metal steel substrates occurs, the local pH increases and nanocontainers release their content.[141,142] Corrosion inhibitors including benzotriazole, dodecylamine and imidazole have been successfully released by using this approach.[140,143,144] This LbL-based strategy is promising since it refrains the inhibitor molecules to damage the coating while providing intelligent release properties. Recently a class of multifunctional nanocontainer-loaded coatings has emerged.[145,146]

1.3- Electroactive LbL for biosensors and energy

The exceptional versatility of the LbL approach allows co-immobilization of a large variety of biomolecules and conductive species on surfaces. This has resulted in the

development of numerous applications for catalysis, sensors and energy.[147–149] This following section of this review is focused on recent achievements in the fields of biosensors and energy-related devices.

1.3.1 Electroactive LbL films for biosensors

Elaboration of biosensors requires immobilization of transducing biomolecules in an environment that not only preserves their activity but also ensures communication with the electrode.[150–152] For instance, the activity of glucose oxidase (GOx) was better maintained when the enzyme was terminating chitosan/GOx multilayer films.[153] In contrast, when GOx was combined with a chitosan/PSS multilayer film, this enzyme could reach the same activity as in solution.[154] This result demonstrates the promise of LbL films in preserving the activity of biomolecules. In particular, this deposition process can be performed under mild biocompatible conditions. Most of the available LbL biosensors incorporate enzymes, antigens, antibodies or nucleotides (including DNA) as active compounds. Consequently, a large variety of films for detection of pesticide residues and biomolecules has been developed. A summary of recent achievements is presented in table 2.

Table 2: examples of electrochemical sensors based on LbL films. The active biomolecules of each system is given in bold.

Sensors for biomolecules: applications for health monitoring		
<i>Analyte</i>	<i>LbL-platform</i>	<i>Ref</i>
Glucose	Glucose oxidase – PAH/Prussian Blue	[155]
	Glucose oxidase /multi-wall carbon NTs (MWNT)	[156]
	Glucose oxidase –single wall carbon NTs/ PVPOsBp*	[157]
Cholesterol	Cholesterol oxidase /PAH	[158]
	Cholesterol oxidase /PAH/Carbon NTs-gold NPs	[159]
Choline	Choline oxidase /Prussian Blue/ EACC*	[160]
Dopamine	Dermaseptin / nickel tetrasulfonated phthalocyanines	[161]
Ascorbate	Ascorbate oxidase /Au particles	[162]
Urea	Urease /Chitosan/Carboxymethylpullulan/Polyaniline	[163]
Sensor for pesticide residues: applications for water quality control		
<i>Analyte</i>	<i>LbL-Platform</i>	<i>Ref</i>
Carbofuran	Acetylcholinesterase /dendrimers polyamidoamine -Au/Carbon NTs	[164]
Trichlorfon	Acetylcholinesterase /Poly-DADMAC*	[165]
Carbaryl	Acetylcholinesterase /Poly-DADMAC /Carbon NTs	[166]
Catechol	Cl-catechol 1,2-dioxygenase / dendrimers polyamidoamine	[167]
	PSS-Tyrosinase/gold NPs	[168]
Other common sensors: applications for safety devices and fuel cells		
<i>Analyte</i>	<i>LbL-Platform</i>	<i>Ref</i>
Hydrogen peroxyde	Horseradish peroxidase /Gold NPs/Toluidine blue	[169]
	Catalase / 1-(3-Aminopropyl)-3-methylimidazolium bromide/ TiN NPs	[170]
	Hemoglobin /CdS nanocrystals	[171]
Ethanol	Alcohol oxidase /Poly-DADMAC*	[172]

*PVPOsBp: poly[(vinylpyridine)Os(bipyridyl)₂Cl^{2+/3}], *EACC: 6-*O*-Ethoxytrimethylammoniochitosan chloride, *Poly-DADMAC: Poly (dimethyldiallylammonium chloride)

Enzyme containing biosensors. Since numerous enzymes are now commercially available, enzymatic biosensors have been widely studied during the last decade.[173]

GOx based sensors are probably the most studied and are representative of the rising interest focused on enzyme biosensors. First introduced by Ferreira *et al.*, GOx was assembled by the layer-by-layer technique with PAH on a Prussian Blue-functionalized ITO surface. [155] A linear increase in the sensor sensitivity with the number of deposited GOx layers was measured, indicating that enzymes incorporated within the film retained some activity. In that system, the high sensitivity was explained by the small thickness of the film and the incorporation of catalytic Prussian Blue (PB), which allowed the reaction to occur at 0V. Subsequent work involved doping the GOx-containing multilayer with conductive building blocks like gold NPs or carbon NTs to promote electronic communication with the electrode.[152,174,175] Multi-enzyme platforms could also be assembled.[176] Recent work has followed this trend aimed at combining preservation of enzyme activity with catalytic reduction of the operating potential and an enhanced electronic communication within the multilayer.[151][177] The main drawback of this approach is that it relies on the stabilities of enzymes thus limiting the scope of applications. Despite this, enzyme-based biosensor films are, of course, perfectly suitable for biological monitoring. For instance, dopamine sensors are promising candidates for diagnosis and monitoring of Parkinson's disease.[178]

LbL Immunosensors. Incorporation of antigens and antibodies in multilayer films allows the development of sensors with high analyte selectivities. Detection methods for antigen-antibody binding can be established based on optical, electrochemical or weight measurements.[179] In 2006, Zhuo *et al.* reported a sequential approach for electrochemical immunosensing of α -1-fetoprotein (AFP).[180] Initial assembly of a thionine/gold NPs multilayer was followed by post-functionalization with anti-AFP and the remaining adsorption sites were then blocked with horseradish peroxidase. The resulting sensor presented nearly ideal selectivity for AFP with a sensitivity of $1\mu\text{g.L}^{-1}$, and good recycling capabilities. This platform has subsequently been improved by incorporating gold or PB NPs within the film and, more recently, by adsorbing anti-AFP on hybrid chitosan platforms containing gold NPs and TiO_2 -graphene.[181,182] By using a similar approach, Ou *et al.* developed an amperometric detector for carcinoembryonic antigen (CEA).[183] This work opened a way towards clinical diagnosis since a high level of CEA may indicate cancer. CEA detection could be improved by immobilizing anti-CEA on LbL films containing gold-decorated NTs.[184] Another tumor marker, human chorionic gonadotropin, has also recently been the subject of detection using an amperometric LbL immunosensor.[185]

DNA and nucleotide-based biosensors. Incorporation of DNA in an LbL biosensor was first reported by Bayachou and coworkers in 2005.[186] DNA was electrostatically adsorbed on poly-DADMAC coated single-wall carbon NTs. The particles obtained exhibited electrocatalytic activity with a ruthenium complex, explained by the oxidation of guanine bases of DNA by the *in-situ* oxidized ruthenium complexes. When DNA was first damaged by treatment with NO, the electrocatalytic current decreased making this system an indirect sensor for DNA damage.[187] By using this approach, DNA/poly-DADMAC multilayer films allowed detection of DNA damage induced by simultaneous contact with H₂O₂ and nitrite. However, when a layer of horseradish peroxidase was adsorbed on top of the film, no damage could be detected. This result was attributed to the protection provided by horseradish peroxidase which degrades H₂O₂ and obstructs or prevents the formation of reactive nitrogen species from nitrites.[188] Recently, LbL DNA/PLL films containing carboxylic group functionalized carbon NTs were assembled and used to detect electrochemically oxidative damage caused to DNA by cadmium ions.[189]

1.3.2 Electroactive LbL for energy-related devices

Incorporation of a large variety of functional building blocks on electrodes can lead to efficient charge transfer and allows the development of numerous energy-related

devices.[190] This following section of this review will focus on recent achievements in the fields of supercapacitors and water splitting.

Supercapacitors.

Supercapacitors are able to deliver energy at a high charge/discharge rate with good cyclability and fast charge propagation.[191,192] These devices can be classified into two categories: electrical double layer capacitors and pseudocapacitors. Electrical double layer capacitors (EDLC) are based on pure capacitive energy storage, with a high cyclability, a fast charge/discharge but a lower electrical capacitance relying mainly on their surface area. Pseudocapacitors rely on electroactive materials able to undergo a faradic process. They generally can achieve higher capacitances yet their cyclability is reduced, due to degradation of their electro-active centers and structure.

The LbL approach has been used to assemble both of these types of capacitor and the corresponding performances are summarized in tables 3 and 4.

Table 3: performances of EDLC supercapacitors.

LbL multilayer films for EDLCs				
<i>LbL type</i>	<i>Electrolyte</i>	<i>Capacitance (F.g⁻¹)</i>	<i>Performance after n cycles</i>	<i>Ref</i>
(MNS/PEI) ₁₀	2 M KCl	288	90.5% (1000 cycles)	[193]
MnO ₂ on MWNT-COO ⁻ /MWNT-NH ₃ ⁺	0.1 M K ₂ SO ₄	290	88.5% (1000 cycles)	[194]
MWNT-COOH/MnO _x	PVA-H ₃ PO ₄ gel	Unknown	88.3% (10 000 cycles)	[195]

		50 F cm ⁻³		
SWNT-COOH / SWNT-NH ₃ ⁺ + heat	1 M H ₂ SO ₄	151	Unknown	[196]
(Graphene/azo-polyelectrolyte) ₉	1 M Na ₂ SO ₄	49	Unknown	[197]
SRGO/ PSDAS	1 M Na ₂ SO ₄	150	97% (10 000 cycles)	[198]
RGO/magnetite	1 M NaCl	151	85% (1000 cycles)	[199]
graphene oxidized/ p-phenylenediamine	1 M Na ₂ SO ₄	282	92% (1000 cycles)	[200]
Other EDLC supercapacitors				
<i>Type</i>	<i>Electrolyte</i>	<i>Capacitance (F.g⁻¹)</i>	<i>Performance after n cycles</i>	<i>Ref</i>
Mesoporous carbon nanofibers	1 M KOH	90-152	Around 100% (1000 cycles)	[201]
NiO ₂ /SWCNT/Ionic liquid	-	54	Unknown	[202]
RGO/PMMA	1 M Na ₂ SO ₄	290	85% (1000 cycles)	[203]
RGO/ Filk fibroin	6 M KOH	256	96% (10 000)	[204]

EDLC supercapacitors by LbL process. As early as 2003, the LbL elaboration of silicon oxide semiconductors for EDLC-type capacitors was reported by Hua *et al.*[205] In that system, silicon dioxide was used as an active building block, allowing both surface patterning and optical transparency.[206,207] In 2008, manganese oxide nanosheets (MNS) were incorporated into (MNS/PEI)₁₀ multilayers.[193] The resulting films exhibited pure double-layer capacitive properties reaching 288 F.g⁻¹ with only 9.5% loss of capacity after 1000 cycles within the potential window from 0 to 940 mV (*vs* Ag/AgCl). These results were attributed to the film microstructuration and to the

semi-conductive nature of manganese oxides, which improves electronic transfer through the multilayer compared to purely organic LbL films. Later, it was demonstrated that the incorporation of conductive NPs greatly improves the conductivity of LbL films, opening the route for more complex porous functional coatings.[208,209] Incorporation of multiwall carbon nanotubes in a MWNT-NH₃⁺/MWNT-COO⁻ LbL multilayer film was reported by Hammond and coworkers in 2010.[194] The resulting coating could be post-functionalized with MnO₂ by simple dipping into a MnO₄⁻ solution followed by a reduction step. This concept was applied for the preparation of electrode microarrays, achieving a high performance stability even after 10,000 cycles.[195] Later, Huang and coworkers demonstrated that single-wall NTs could also be incorporated in LbL supercapacitors.[196] When the corresponding films were heated at 300°C under H₂, the NTs could be unzipped, leading to graphene thus improving the capacitive performances.

Recently, the design of graphene based supercapacitors has attracted substantial interest.[210] In 2011, rather modest performances were reported by Wang *et al.* for a graphene/azo-polyelectrolyte system.[197] Also, when sulfonated reduced graphene oxide (SRGO) was combined with polystyrene-based diazonium salt (PSDAS), a specific capacitance of 150 F.g⁻¹ was achieved with a performance retention of 97%

after 10,000 cycles.[198] In another very recent study, RGO was associated with magnetite in an LbL film, leading to LbL supercapacitors with similar capacitances.[199] Again very recently, Sk and Yue could achieve 282 F.g^{-1} by using a graphene oxidized/ p-phenylenediamine multilayer. [200] When compared with other graphene or carbon based EDLC supercapacitors, LbL-based devices perform in a similar way, suggesting that their internal structure allows a good electronic communication (table 3). However, literature regarding EDLC supercapacitors describes very heterogeneous performances, making comparisons difficult.

Table 4: performances of pseudocapacitors.

LbL multilayer films for pseudocapacitors				
<i>LbL type</i>	<i>Electrolyte</i>	<i>Capacitance (F.g^{-1})</i>	<i>Performance after n cycles</i>	<i>Ref</i>
MNS/Poly-DADMAC/MWCNT	0.1 M Na_2SO_4	581	Unknown	[211]
(MWCNT/Co-Ox flakes) ₃	0.1 M Na_2SO_4	802	Unknown	[212]
MWCNT/PANI	1 M LiPF_6	417	96% (1000 cycles)	[213]
GO/PANI	1 M H_2SO_4	375	91% (500 cycles)	[214]
Other polymer based pseudocapacitors				
<i>Type (preparation method)</i>	<i>Electrolyte</i>	<i>Capacitance (F.g^{-1})</i>	<i>Performance after n cycles</i>	<i>Ref</i>
PANI and carbonaceous shell (electropolymerization)	1 M H_2SO_4	190	95% (10 000 cycles)	[215]
Doped PANI (reverse pulse voltammetry)	10^{-3} M HCl and 1 M KCl	480	Unknown	[216]
CNT/polypyrrole/ MnO_2 (chemical polymerization)	1 M Na_2SO_4	281	88% (10 000 cycles)	[217]
MWCNT/PANI	0.1 M H_2SO_4	560	71% (700 cycles)	[218]

Polypyrrole/sodium carboxymethylcellulose nanosphere	1 M Na ₂ SO ₄	184	80% (200 cycles)	[219]

Pseudocapacitors by LbL process. In 2009, the combination of metal oxide nanosheets (MNS) with MWCNT and Poly-DADMAC allowed a maximum specific capacitance of 581 F.g⁻¹ to be achieved.[211,220] This high value could partly be explained by a faradic current during charges/discharges, owed to the redox behavior of manganese oxides. Similar experiments with cobalt oxides in place of manganese oxides led to a capacitance of 802 F.g⁻¹. [212] Electroactive polyaniline (PANI) has been extensively used in the design of pseudocapacitors. In 2011, the group of Hammond combined PANI with MWCNT reaching a pseudocapacitance of 417 F.g⁻¹ with an excellent stability.[213] Similar LbL platforms were later reported by associating PANI with GO and RGO.[214,221,222] These systems lead to similar pseudocapacitance performances, with good retention of capacitance of up to 93% of the starting value after 1000 cycles. Recently, Shao and coworkers developed PANI nanofibers/vanadium pentoxide LbL films, resulting in significant gains in capacitance compared to systems based on regular PANI.[223–225] Compared to conventional polymer-based pseudocapacitors, LbL-based pseudocapacitors reach honorable capacitance performances but their cyclability has still not been extensively studied (table 4).

Water splitting

During the last decade, water evolution reactions induced by photocatalysis or electrocatalysis have attracted great interest from the research community since it could be used to develop replacement technologies for non-renewable energy sources.[226–229] Surprisingly, very few attempts have been made to achieve water splitting using the LbL platform although they have been frequently used for triggering other reactions.[230,231] In 2013, the group of Zhao reported LbL assembly of Co_3O_4 NPs/graphene composites[232] with the resulting films exhibiting better physical stabilities and catalytic activities than the pristine catalysts both for the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR). For OER, the faradic efficiency of the film reached 95% and 75% of the catalyst efficiency was preserved after 5h of bulk water electrolysis. A similar approach was reported by Huang *et al.* in 2014.[233] A multilayer film composed of alternating RGO and cobalt porphyrin allowed efficient hydrogen evolution reaction with only a slight decrease in activity after 1000 cycles. The number of deposited layers influenced the device performance with an optimum at 7 bilayers. The remarkable catalytic activity of this

multilayer film was attributed to the the Co-N₄ center in the porphyrins. Similar results were achieved when Ru-substituted polyoxometalate and Ru-mettallodendrimers were deposited on Poly-DADMAC modified carbon electrodes.[234] By using a different strategy, Wessling and coworkers assembled catalytic PEM in a bipolar membrane device (figure 7).[235] When a PEDOT-PSS/PEI multilayer was deposited on a bipolar membrane, the modified device achieved a water splitting capacity close to 90% of that of a commercial membrane FBM (FuMA-Tech, Germany). Both the ionic strength and the number of deposited layers were found to be critical for the catalytic performance. This research field would probably greatly beneficiate from a better understanding of the Donnan potential and the ionic distribution within polymer films, as previously discussed. In 2014, the same group demonstrated that the PEI layers, containing catalytic imine functions, are a key component for enhancing water splitting on membranes, yet a precise mechanism has yet to be described.[236]

Figure 7: LbL modified bipolar electrodes for water splitting. LbL deposition of a PEDOT:PSS/PEI multilayer on the anion exchange part of a bipolar membrane, conjugated with casting of its cation exchange layer part with sulfonated poly(ether ether ketone) (SPEEK) could significantly reduce the electric potential required for water splitting.[236]

2- Advanced electrochemically engineered films

Recently, various methods of film synthesis by using electrochemical processes have been reported. The resulting surface platforms may either compete or be combined with the LbL approach in the future of complex surface engineering science. In combination, the electrochemical stimulus can be seen as a trigger for the film buildup and/or its functionalization. The second part of this review paper will be devoted to electro-triggered film formation with special emphasis on the utility of electroclick and carbazole coupling reactions.

2.1- Pioneering works

Electrochemical methods were for long considered as ideal for surface analysis and stimulation of polymer coatings. In contrast, they have been recently considered as triggers for electrosynthesis, including covalent coupling between functional building blocks. New approaches could thus emerge for achieving both the deposition of films and their functionalization.[27] One aspect of this research has consisted of studying how application of an electric field can improve non-covalent film deposition, while another strategy has focused on electro-triggering of covalent reactions.

Non-covalent film deposition enhanced by electrochemistry. Initially introduced by the group of Van Tassel, the application of an electric field during LbL deposition has been proven as a convenient way for accelerating the assembly of polyelectrolyte multilayers. In 2003, Brusatori *et al* reported that application of positive potentials between 1 and 2 V could increase albumin and cytochrome C adsorption on ITO substrates.[237] In that case, a single layer deposition of proteins could be performed and higher voltages lead to larger adsorptions in water. The growth of the resulting films was monitored by using optical waveguide light-mode spectroscopy,[238] UV spectroscopy,[239] electrochemical-QCM,[240,241] and plasmonic sensors.[242] Later, electro-assisted

LbL depositions of PSS/PAH and Dextran/PLL films were found to be favored by application of potentials between 1 and 2 V.[243] Adsorption masses of individual polycations were increased by 60 % (PAH) and 500 % (Dextran). Dextran/PLL LbL films grew at 70% faster rates. A generalization of this strategy to single step deposition of amine containing macromolecules was demonstrated in 2007 by Ngankam *et al.*, introducing significant possibilities for the design of biocompatible surfaces. [244] For instance, electrodeposition of chitosan was reported as early as 2003 and widely and successfully adopted by the biomaterial research community.[245–248] In that case, an increase of the local pH caused by reduction of protons (to dihydrogen) seems to play a significant role during the deposition process.[249] It permitted the design of a wide variety of biological and electrochemical sensors, patterns and layered materials.[250–254] One of the major drawbacks of this method is the use of large potentials, which limits the range of its applications. A large number of studies have been undertaken in attempts to elucidate the mechanism that drives electrodeposition of polyelectrolytes and proteins, although a full understanding has yet to be achieved. It seems to result from an interplay between molecular conformation, electrostatics, Van Der Waals (VdW) interactions and entropic effects. Charged domains on macromolecules and VdW interactions were initially thought to be the main driving

forces. Indeed, initial attempts to study this phenomenon revealed that adsorption rates of polyelectrolytes increased with both the potential and the ionic strength, while increases in the pH resulted in a bell-shaped growth curve suggesting that moderately random coil conformations of polymers would be more favorable.[244] However, the parameters involved are not totally independent, complicating the discussion.[255] For instance, electrodeposition of a PAA/PAH film was recently found to be favored by a stretched chain conformation.[256] Polarization of macromolecules by an external electric field also seems to restrict the distribution of their adsorption orientation, improving the film growth.[257,258] However, increasing the magnitude of the applied potential leads to controversial effects in the film construction. Ko *et al* have attempted an explanation by invoking the competition between electrolysis of water and electrophoretic deposition of polyelectrolytes during application of a potential.[259]

Covalent reactions enhanced by electrochemistry. Some chemical functions such as hydroquinones or thiols allow covalent coupling between complementary molecules when an electrical potential is applied.[260,261] These approaches have allowed the design of (bio)sensors and patterned surfaces, although they are not currently used to assemble non-polymerized films or LbL platforms.[262–265] Successful covalent

reticulation of polymer films by application of an electric potential was first reported by Zhang and coworkers.[266] $\text{Os}(\text{bipyridine})_2\text{Cl}_2$ and $\text{Ru}(\text{bipyridine})_2\text{Cl}_2$ complexes were used as linkers and were electrochemically activated by a reductive potential, resulting in their covalent coupling with amine functionalities contained in the applied polymers.[267–269] Reduction of the metallic center weakens the M-Cl bond and favors its exchange bonding with amines. For instance chitosan chains could be crosslinked with this approach by applying -1.5 V (*vs* Ag/AgCl) for 5 minutes (figure 8), allowing immobilization of enzymes by coordination covalence with a better retention compared with non-covalent electrodeposited chitosan films.

Figure 8: Electrochemistry as a trigger for covalent reticulation. Covalent reticulation of polymers by electroactivation of $\text{Ru}(\text{bipyridine})_2\text{Cl}_2$ as a linker. [266]

Local linker electroactivation was recently extended to homobifunctional organic molecules by the group of Schuhmann.[270] Electro-induced pH-shifts were used to

in-situ deprotect the linkers, leading to the growth and covalent crosslinking of functional redox polymers. Appearance of these various electro-controllable cross-linking strategies introduces significant possibilities for the design of multifunctional polymer platforms grown from a single solution.

2.2 Carbazole covalent coupling and ECC-LbL

Prior to the great success of the introduction of the LbL approach, electropolymerization, from a fundamental point of view, had already become one of the key methods allowing elaboration of molecular matrices. *In-situ* electropolymerization provides access to uniform polymeric films on conductive substrates with tunable morphologies and thicknesses.[271] However, over the past few decades, electropolymerization has been limited to applications such as electrochromism and conductive films where ion-doping is required.[272–276] Indeed, non-quantitative unlimited electrochemical coupling reactions usually lead to conducting conjugated polymers with high doping states. In fact, polymers are often unnecessary or disadvantageous. For instance, when electropolymerization of thiophene-appended C₆₀ was studied, the expected functionality arising from C₆₀ moieties was largely suppressed by the highly doped polythiophene.[277] Carbazole functional groups have been extensively studied with

regards to both their covalent coupling and polymerization abilities. They have thus been used as reticulation points both during the assembly of polymer films or in post-construction treatments.

2.2.1 Post-construction reticulation.

The group of Advincula studied how carbazole- and thiophene-containing precursors can be *in situ* electro-polymerized, forming reticulated polymer films.[278–280] In 2007, an LbL film composed of alternating layers of anionic poly{[2-(thiophen-3-yl)ethyl methacrylate]-*co*-[methacrylic acid]}, P(TEM-*co*-MA) and cationic poly[4-(9*H*-carbazol-9-yl)-*N*-ethyl-*N,N*-dimethylbutan-1-aminium bromide] was obtained.[281,282] The resulting multilayer could be crosslinked by covalent electropolymerization between the carbazole and thiophene units when an electrochemical potential between 0 and +1.5 V was applied (reference Ag/AgCl). This method was subsequently generalized to different types of thiophene and carbazole bearing polymers.[283,284] Recently, this process has been extended to carbazole-carbazole coupling and patterning of LbL coatings,[285,286] allowing the design of hybrid films containing embedded CdSe nanocrystals as p-n junctions on ITO.[287]

Figure 9: Comparison of conventional electropolymerization and carbazole electrocoupling. Oligomer formation allows an improved control of the functionalization, in contrast, polymerization generally leads to better doping states and conductivities.

2.2.2 Coupling during film buildup.

Li and Ariga developed a quantitative electrochemical reaction of N-alkylcarbazole (Figure 9a),[288] which leads to oligomers and prevents formation of a conducting conjugated polymer (Figure 9b). This strategy allowed interconnection of functional building blocks through N-alkylcarbazole as a bridge linker for film elaboration. The resulting di-N-alkylcarbazole, unlike other electropolymerizable precursors such as aniline and thiophene, is transparent in the visible light region. When C₆₀ bearing carbazole groups were used, the resulting polymer films exhibited a low doping level and the intrinsic physicochemical properties of C₆₀. Easily controllable thickness and

patternability could be observed by AFM and SEM observations. This approach fills a void that existed for electrochemical preparation of non-conjugated polymers. It significantly broadened the range of potential applications of electrochemical synthesis to a large library of molecules, building blocks, nanoparticles with a high degree of control over molecular structures.

Figure 10: One-pot alternating electropolymerization. Reductive and oxidative electropolymerizations of the two components take place in the same solution and leads to an LbL film. [288]

Combination of carbazole and vinyl electropolymerizations allows one-pot LbL assembly by alternation of reductive and oxidative electrochemical reactions.[289] A mixture of $[\text{Ru}(\text{bpy})_2(\text{dvbpy})]$ (bpy: 2,2'-bipyridine; dvbpy: 5,5'-divinyl-2,2'-bipyridine) and a carbazole containing 9,9'-spirobifluorene derivative was used. Reductive and

oxidative radical-radical electrochemical reactions occurred at vinyl groups in the Ru complex and at carbazole groups respectively, when reductive and oxidative potentials were applied (figure 10). Formation of carbon-carbon single bonds and biscarbazole moieties in the two components did not impair the optical or electronic properties of the resulting films. This method represents an easy route to one-pot LbL incorporation of a wide library of carbazole and vinyl containing building blocks, including gold nanoparticles for hybrid photoelectric devices.

2.2.3 Electrochemical-coupling layer-by-layer (ECC-LbL).

Li and Ariga combined the electro-oligomerization reaction of N-alkylcarbazole with the concept of layer-by-layer assembly, developing the electrochemical-coupling layer-by-layer (ECC-LbL) approach (Figure 11).[290] By using various carbazole derivatives carrying distinctive donor (porphyrin and fluorine) and acceptor (fullerene) moieties, the formation of ECC-LbL assemblies with controllable optical and electrical properties was demonstrated. The ECC-LbL process was controlled by applying electrical commands at the electrodes allowing surface patterning. For instance, different messages could be drawn by selectively depositing a multilayer on ITO thanks to individual activation with a working electrode.[291] A selective fluorescent display

was also demonstrated through efficient energy transfer between neighboring layers of fluorenes (energy donor) and fullerenes (energy acceptor). Area-selective LbL assembly in patterning mode could be performed by varying the spatial application of voltages.

Figure 11: Electrochemical coupling layer-by-layer (ECC-LbL). Carbazole-bearing building blocks are coupled electrochemically to the film at each deposition step. [290]

2.2.4 Applications of carbazole electrocoupling and EC-LbL.

In general, electropolymerized conjugated polymers exhibit weak or no fluorescence, probably due to structural defects and quenching by doping counterions in the film.[292,293] Advincula and co-workers reported a luminescent thin film of conjugated polymer with pendant N-alkyl carbazole. It was achieved by electropolymerization between electroactive carbazole units substituted on polyfluorene.[294] The large difference in the oxidation potential between polyfluorene

and the carbazole unit ensures selective electropolymerization of carbazole groups without affecting the polymer backbone. Fluorescence from these films exhibited a moderate emission band at 530 nm which may be due to aggregation of polyfluorene chains and structural defects, such as ketonic and charge doped species. Subsequently, a trifluorene polymer possessing strong blue fluorescence and containing peripheral carbazole units was synthesized.[295] Well-defined structure and controlled electrochemical fabrication lead to a strongly blue luminescent film with smooth surface morphology and excellent thermal stability. When incorporated as the light emitting layer in OLEDs, these films exhibited better performances (brightness of 4224 cd/m² and efficiency of 0.47 cd/A) than devices fabricated by spin-coating (brightness of 78 cd/m² and efficiency of 0.11 cd/A). Elaboration of highly luminescent films by electrochemical synthesis using rational molecular design and controlled electrochemical deposition was thus demonstrated.[296–298] Ma and coworkers reported highly efficient blue LEDs based on polymer[299] and white LEDs based on small molecules.[300,301] The latter typically exhibited the best performances with a luminance efficiency of 6.7 cd/A and brightness of $\sim 10^5$ cd/m². Micrometer-size addressing at a well-defined electrode could be performed. It provided a new fabrication method for micropatterned polymeric electroluminescent devices, and has the advantage

of simplicity over current techniques such as ink-jet printing and shade masking.[302,303] Full-color micropatterned LbL films with sharp edges and high resolution could be prepared on ITO. In principle, it could be extended to the assembly of “RGB color pixels” by applying “on” and “off” potentials on the ITO strip and by loading the electrolytic cell with various color precursors.[304] Surface patterning was also performed by using ECC-LbL.[291] Another application of ECC-LbL films in thin-film photoelectronics was demonstrated using a prototype p-n heterojunction device with an ITO-porphyrin(donor)-fullerene (acceptor)-Al structure.[291] While the dark current remained almost constantly zero, the anodic photocurrent increased monotonically with increasing positive bias at the ITO electrode. The work function of fullerene films could be freely controlled between 3.7 and 4.3 eV.[305] These films were successfully employed in an inverted solar cell leading to significant PCEs up to 6.3%. ECC-LbL could also be coupled with products of top-down nanotechnology such as highly miniaturized integrated circuits. Therefore, this assembly method might be a powerful way to fabricate robust and well-designed organic devices.

Figure 12: ECC-LbL with nanoparticles for solar devices. Carbazole-bearing gold NPs were immobilized electrochemically with an organic linker, allowing various thin film configurations and solar-cell designs. [306]

By utilizing ECC-LbL assembly with inorganic gold functional nanoparticles and small organic linkers, thin films could be obtained (Figure 12).[306] Each individual layer could be quantitatively tailored by applying a number of CV cycles, allowing the tuning of the distribution of gold nanoparticles. This work represented a significant improvement compared to films prepared using polar solvents.[307–313] The elaboration of inorganic and small organic hybrid films is usually challenging because of the tendency of nanoparticles to be irregularly distributed and/or agglomerated.[314,315] In this case, the gold film was transparent, conductive, and could be used as an electrode device. By changing the device architecture, ECC-LbL lead also to an economical route for assembly of both the photoactive layer and the

electrode of a cell model (Figure 12).

2.2.5 Conclusion and Challenges:

Carbazole coupling and ECC-LbL can be used to organize small molecules, polymers, metal complexes, and nanoparticles into ordered thin films. This general feature also enables combination of most materials into films with well-defined layer structures and functions. Although many improvements are required before practical applications can be achieved, these films have already presented excellent performance in LEDs and photovoltaic devices. One challenge relies on using or depressing the effect of electrochemical doping while performing ECC-LbL. Indeed, combining this approach with standard electrochemical platforms would allow the design of versatile electro-active films on complex or three-dimensional substrates. For instance, free-standing films could be developed by ECC-LbL assembly.

2.3 Electroclick method

2.3.1 Emergence of electroclick chemistry

Initially discovered in 1893,[316] covalent coupling between azide and alkyne functions

was identified as a cycloaddition reaction in 1963 by Rolf Huisgen.[317] In spite of being thermodynamically favorable and remarkably orthogonal with respect to unwanted reactions, the Huisgen cycloaddition originally required heat and pressure (and the related safety precautions) for its implementation.[318,319] It remained thus uninvestigated until Sharpless highlighted it in 2001 as a key reaction for achieving modular molecular design with broad applicability and harmless byproducts: the click chemistry concept.[319] A year later, the Huisgen dipolar cycloaddition gained both speed and regioselectivity when Meldal and Sharpless groups reported that the reaction could be catalytically promoted by using Cu(I) ions.[320,321] The resulting “Copper(I)-catalyzed Alkyne-Azide Cycloaddition (CuAAC)” can be used to efficiently form 1-4-disubstituted 1,2,3-triazole bonds in water and organic solvents, over wide ranges of pH (4 to 12) and temperature (0 to 160°C).[322–324] Based on success of CuAAC, a large library of commercially available “clickable” molecules has been developed, enlarging the application fields of click chemistry.[325] To perform CuAAC, catalytic quantities of Cu(I) ions are introduced by using Cu(I) salts or by *in-situ* reduction of Cu(II) with sodium acetate. Other triggers for generation of the requisite Cu(I) cations include UV-irradiation,[326,327] ultrasound,[328] microwaves[329,330] and electro-chemical[331] stimuli. This latter electrochemical approach allows a

reagent-free functionalization of surfaces and has met with great interest in the research community. In fact, the technique has become known by its own special name: “electroclick” chemistry.[332] By applying a mild reductive potential (-150 mV to -500 mV vs Ag/AgCl) to a substrate in contact with a Cu(II) solution, catalytic Cu(I) ions and Cu_{metal} can be obtained by several routes:[333]

Cu_{metal} formation can be avoided by complexation of Cu(II) with stabilizing ligands such as bis(bathophenanthroline)disulfonic acid[331,334] although presence of Cu_{metal} can also be advantageous since it also catalyzes the click reaction, opening the route toward “spontaneous” click chemistry.[335–338]

2.3.2 Electroclick on monolayers

Electroclick functionalization of “clickable” azido and alkyno-terminal monolayers was the initial achievement in this field, probably due to the proximity of reactive groups

with the electrode which allows an easy detection of the electroclick efficiency. Most studies use cyclic voltammetry (CV) and fluorescence microscopy to determine the electroclick immobilization of active molecules. Attenuated total reflectance infrared spectroscopy (ATR-IR) and X-ray photoelectron spectroscopy (XPS) can also be used to follow the click reaction.[339,340] In 2006, Devaraj *et al.* were the first to report selective activation and deactivation of Cu(I) catalyst by application of -300 mV (*versus* Ag/AgCl) to the substrate, leading to covalent electroclick of ethynylferrocene on an azido-terminal self-assembled monolayer (SAM) (figure 13).[331,341,342]

Figure 13: Principle of electroclick chemistry. Controlled electroclick reticulation of an ethynylferrocene onto an azido-terminal SAM. Application of a -300 mV potential (*versus* Ag/AgCl) in presence of Cu(II) ions induces the generation of Cu(I) ions which catalyzes the click coupling. [331,341,342]

Electroclicking ferrocene on SAMs[343] allowed electrochemical sensing of Cu(II) ions in water and dairy products down to low concentrations of 10^{-14} M.[344] However, this

strategy relies on S-Au bonds for grafting onto the surface which tend to oxidize in air and other media, and also only allow for a narrow potential stability window. Monolayer stability for electroclick is greatly improved by using dithiol phosphoramidite (DTPA) moieties. Ripert *et al* demonstrated that this approach is suitable for oligonucleotide immobilization, allowing fluorescence microscopy visualization of the functionalized area.[345] This work opened the way toward protein electroclick on SAMs, which was performed recently with azide-bearing biotin.[346] A variant of the SAM electroclick functionalization has been extensively developed by the group of Le Mest where Cu(II) ions were directly complexed to clickable molecules, allowing their “self-induced” electroclick reticulation on SAMs (figure 14).[347,348] This surface immobilization of copper complexes lead to tunable electron transfer and electro-catalytic activity.[349,350] The main advantage of this technique is due to the absence of copper salt in solution, which would cause interference with biological materials. Its drawback is the required synthesis of functional clickable molecules able to complex Cu(II) ions.

Figure 14: Self-induced electroclick chemistry. Rather than using potentially bio-disturbing free Cu(II) ions in solution, copper ions are trapped on the functional molecules to be clicked. [347,348]

Recently, another type of monolayer has been used to achieve electroclick functionalization. Phenylazide was electrografted onto glassy carbon by using diazonium chemistry, offering an ideal surface platform for electroclick of an alkyne functionalized human IgG.[351] A detection sensitivity of $3 \times 10^{-11} \text{ g mL}^{-1}$ was obtained for anti-human IgG. The effectiveness of this concept is promising for the development of electroclick-designed immunosensors.

2.3.3 Electroclick functionalization of polymer platforms

Compared to functional monolayers, polymeric platforms offer robustness, versatility and thickness control, conferring on them an unprecedented range of applications. Their electroclick functionalization was achieved as early as 2009 by Hansen *et al.*[332] In

order to avoid prior synthesis of monomers and polymers bearing clickable functions, Bartels *et al* introduced a multistep elaboration of polymeric platforms.[352] Electrodes were first spin-coated with agarose that allowed functionalization with acetylene groups using a base-catalyzed esterification reaction. The alkyne bearing agarose film then underwent electroclick with an azide bearing pyrene in DMF when a potential of -2.4V was applied (*versus* Pt) in the presence of CuSO₄. This approach opens the way for uses of electroclick involving bio-sourced and bio-compatible materials. Thus, the first example of protein functionalized bio-polymer platforms using electroclick was recently reported. A chitosan film modified with alkyne groups was successfully electroclicked with azide-tagged Bovine Serum Albumin.[353]

2.3.4 Electroclick as a buildup stimulus for polymer platforms

Instead of focusing on electroclick functionalization, the team of Schaaf and Boulmedais investigated how this approach could be used to induce a film buildup.[27] In 2010, they reported an all-polyanionic LbL film assembly, composed of PAA bearing alkyne (PAA-C≡CH) or azide (PAA-N₃) functions.[354] Electroclick reticulation could be performed at each deposition step by applying -350 mV (vs Ag/AgCl) in the presence of CuSO₄. The resulting covalent film swelled reversibly in response to pH changes,

indicating charge tuning abilities in the polymer matrix. Contrary to regular LbL films, no spontaneous interaction between polymer chains was required to assemble multilayer films by electroclick. PAA-N₃, PAA-C≡CH could thus be mixed in a single CuSO₄ solution and a single-step film deposition was achieved when electroclick was performed by applying an electrochemical potential between -350 mV and +600 mV (vs Ag/AgCl) (figure 15).[340] Morphogenesis of films obtained by using this *one-pot morphogen driven self-construction* approach could be controlled by Cu(I) ions diffusion. Increasing the number of constructing CV cycles resulted in thicker coatings.

Figure 15: One-pot morphogen driven self-construction of a polymer film. Clickable functional polymers are mixed in solution and react together only close to the surface, where Cu(I) ions are electrogenerated from Cu(II) in solution. [340]

This concept was extended to clickable polycations,[340] and mixtures of functional polymers reticulated with homobifunctional linkers.[355] The robustness of one-pot electroclick morphogen driven self-constructing films allowed the assembly of a large variety of polymer platforms. For instance, coatings whose cohesion relied on host-guest interactions were obtained from a (PAA-N₃, ethynylferrocene, ethynyl β -cyclodextrin) mixture.[356] In that case, both controlled film dissolution and reversible trapping of hydrophobic molecules could be performed. By using a (PAA-N₃, ethynylferrocene, β -cyclodextrin) mixture, supramolecular polyrotaxane films were self-constructed.[357] In this system, electroclick was used to lock the polyrotaxane geometry, allowing their spontaneous self-assembly by non-covalent interactions. Recently a further step toward one-step elaboration of biocompatible coatings was achieved by applying the electroclick morphogen driven self-construction concept to azide and alkyne bearing chitosan.[358] Polymer brushes obtained by atom transfer radical polymerization could also recently be assembled by electrogenerating Cu(I) ions.[359]

2.3.5 Conducting polymers and electroclick

Combination of electroclick with conducting polymer platforms has attracted a focused

attention since it promises applications for organic light-emitting diodes (OLEDs), sensors, and polymer solar cells, where good electrical conductivity and easy functionalization are crucial.[360] Films composed of poly(pyrrole),[361] poly(thiophene),[362] PEDOT,[363] and PANI [364–366] have been functionalized by standard CuAAC. Both activity of the clicked molecules and conductivity of the polymer coating could be preserved.[363,367] However, to our knowledge, only PANI and PEDOT based films have been used to perform electroclick. Post-functionalization of PEDOT films was extensively studied by the group of Larsen.[332] Micrometer-scale electrodes were coated with poly(3,4-(1-azidomethylethylene) dioxothiophene) (PEDOT-N₃) and electroclicked with alkynated fluorescent probes. Efficient coupling could be achieved by applying a range of negative potentials (-0.5 V to -2 V) during 15 minutes in DMF in the presence of Cu(II). A PEDOT-N₃ film could also be deposited on poly(azido-styrene) and partially dissolved, leading to patterned platforms that can be functionalized either by using “regular” click chemistry on the poly(azido-styrene) substrate or by electroclick on PEDOT-N₃. [368] In 2014, Ipek *et al* were the first to describe the electroclick post-functionalization of poly(4-azidoaniline) (PANI-N₃) coatings.[369] An alkyne bearing cobalt phthalocyanine was successfully coupled to the polymer film, allowing

detection of eserine. Recently, this system has been tested for a wide range of pesticides, demonstrating good linearity and detection limits much lower than the maximum residue limits defined in the European Union pesticides database.[370] Since PANI is a conductive, inexpensive, chemically and thermally resistant polymer, its electroclick functionalization is expected to find numerous applications in sensing, fuel cells and energetic devices.[371–374] However, its post-functionalization does not take advantage of PANI chains ability to self-organize into a variety of supramolecular structures.[375–377] To solve this issue, Rydzek *et al* recently introduced the *Simultaneous Electropolymerization and ElectroClick functionalization (SEEC)* of PANI (figure 16).[378] Highly versatile films could be obtained by applying an electrochemical stimulus between -0.6V and +0.9 V (vs Ag/AgCl), to a substrate dipped into a solution of clickable monomers and functional molecules. Both the film morphology and activity could be tuned, by changing the electropolymerization condition and electroclicked molecules (figure 16b). Promising pseudocapacitance and biocatalytic activities could be achieved, suggesting that the *SEEC* process will play a significant role in fields as diverse as sensors, fuel/energetic devices, biomaterials, or stimuli-responsive coatings. Recently, electroclick and *SEEC* were performed by Maringa *et al* by using azidoaniline and ethynylpyridine.[379] The obtained films could

be post-functionalized with iron tetracarboxyphthalocyanine and were tested for hydrazine electro-oxidation.

Figure 16: Simultaneous Electropolymerization and ElectroClick functionalization (SEEC). (a) Clickable electroactive monomers can be simultaneously electropolymerized and electroclicked with functional building blocks in presence of a Cu(II) salt. Depending on building conditions, the coating morphology can be adjusted from (b) fibrillar to (c) globular topographies. [378]

2.3.6 Functionalization patterning by using electroclick

Electroclick is fast, specific, and occurs under mild conditions, providing thus an ideal coupling reaction for surface patterning. Electrochemically generated gradients recently became a hot topic.[380] Electroclick perfectly matches with this concept since a spatial control of Cu(I) ions generation results in a patterned functionalization. Cu(I) ions are indeed unstable in the presence of dissolved oxygen, which restricts their diffusion

and permits the coupling reactions to occur only close to the electrode. Consequently, micro-electrodes,[331] local probe microscopies,[381,382] bipolar electrodes[383] and gradient devices[384,385] have been used to locally induce electroclick as described on figure 17.

Figure 17: Patterning strategies for electroclick. Local generation and propagation of Cu(I) catalytic ions can be triggered by (a) microelectrodes, [331] (b) local probes, [381,382] (c) electrogenerated gradients, [384,385] and (d) bipolar electrochemistry. [383]

Microelectrode patterning. Initially introduced by Devaraj *et al.*, [331] electroclick patterning by using microelectrodes has historically been very popular for monolayer

functionalization. In that case, the surface of microelectrodes is directly modified and their size defines the patterning resolution (figure 17a). Devaraj *et al* demonstrated the concept by electroclicking ethynylferrocene on an azido-terminal SAM with a 10 μm resolution.[331] By using a similar approach, Canete *et al* elaborated an E-DNA sensor array with each pixel measuring 0.88 mm^2 , and functionalized it with a different stem-loop DNA.[386] This concept has recently been extended by developing interdigitated electrodes allowing detection of both DNA hybridization and protein binding on the patterned surface.[387] Recently, microelectrode electroclick patterning was applied to polymer platforms. Both PEDOT- N_3 and alkyne- containing chitosan films were coupled with fluorescent clickable molecules, achieving a minimum resolution of 20 μm . [332,353] Simple and generic design of lab-on-a-chip devices is expected.

Patterning by using local-probe microscopies. In 2007, a 100 μm wide ultramicroelectrode (UME) from a scanning electrochemical microscope (SECM) was used to locally electroclick a fluorescent dye on azido-terminated monolayers.[382] In that case, the electrode scans the substrate, which can be non-conductive, and functionalize it (figure 17b). Resulting patterned surfaces exhibited respectively

functionalized dots of 300 μm surrounded by outer rings of 500-600 μm . This was attributed to the surface area located directly below the UME and to Cu(I) gradient respectively. However both the size of the UME and its distance from the substrate should affect the patterning resolution. For instance, by using 25 and 12.5 μm diameter UMEs at a distance of 10 μm from the surface, Quinton *et al* could improve the resolution to 75 μm .^[388] In that work, an azido-aryl monolayer was patterned by electroclick with ethynylferrocene, allowing spatially resolved electrocatalysis of potassium ferrocyanide. Recently, reducing the UME diameter and the distance to the substrate to 5 μm allowed 20 μm resolution to be obtained.^[389] When self-induced electroclick was performed on azido-terminal SAMs, immobilization of Cu(I) complexes resulted in an auto-catalytic propagation of the functionalization area, decreasing the final resolution (table 5). At the moment, local-probe based electroclick patterning for polymer platforms has not been reported. Using SECM as a local trigger for electroclick self-construction beyond the monolayer range will probably be the next challenge.

Table 5: Resolution and potential applications of patterned electroclick.

Platforms	Patterning technique	Best resolution (μm)	Applications	References
Azido-SAM	Microelectrode	10	DNA and protein sensors	[331,386,387]

Clickable polymers	Microelectrode	20	OLED, solar cells, Biomaterials	[332] and [353]
Azido-SAM Azido-silane Azido-aryl	SECM	20	Local electrocatalysis	[382,388,389]
Azido-silane monolayer	Electro-generated gradients	50	Biomaterials, cellular migration control	[384,385,390]
PEDOT-N ₃	Bipolar electro-chemistry	unknown	Energetic devices, Biomaterials	[383]

Patterning by controlled electrochemical gradients. Diffusion of copper ions from the area of their generation to the bulk is an issue for fine resolution patterning although it is also a tremendous advantage for functional gradients design. Hansen *et al* were the first to demonstrate how a masked copper electrode could locally generate Cu(II) ions used for spatially-resolved electroclick.[384] Patterning with 200µm resolution on a precoated PEDOT-N₃ substrate could be achieved. Direct control of the Cu(I) ions' diffusion, rather than that of Cu(II), is the key for elaboration of tunable gradients. By using interdigitated microelectrode networks, Krabbenborg *et al* could locally probe by fluorescence microscopy the electroclick formation of mono and bifunctional gradients on azide-terminated silane monolayers (figure 17c).[385] By increasing the electroclick time, both the coverage density and the length of the one-dimensional gradient could be tuned. Typically the functionalization gradient intensity could be reduced by half at a 20µm distance from the electrode after one minute of electroclick. The stabilization of

Cu(I) with tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) allowed for better control of the ionic gradient.[390] As a result, 50µm long gradients could be formed by electroclicking an alkyne-modified biotin on an azido-silanized substrate.[385] These works gave promising insight toward the design of biomedical devices for investigation of physiological processes like polarization and cellular migration.

Electroclick controlled by bipolar electrochemistry. Bipolar electrochemistry has recently become a hot topic.[391] Polarization of the substrate by this approach represents a promising way for surface gradient design. Its application to electroclick was reported recently by Shida *et al.*[383] A PEDOT-N₃ coated bipolar electrode could be functionalized only on its cathodic part and in a gradient manner with various alkyne-bearing molecules (figure 17d).

2.3.7 Conclusion and Challenges:

Electroclick is an emerging approach which is anticipated to contribute to the next generation of interfacial nanomaterials despite most current studies having been focused on proofs of concept.

Electroclick has been shown to be a highly robust and versatile strategy to generate and

functionalize 2D and 3D surface platforms composed of functional monolayers and polymer films. A large range of clickable building blocks has been tested, allowing the elaboration of organic, electroactive, catalytic, and bioactive interfaces. Promising applications have been highlighted in fields including biomaterials, energetic devices and sensors. It is noteworthy that no study using inorganic building blocks to perform electroclick has been reported although that is a promising research direction perhaps for critical improvements in the field of energy devices. Electroclick essentially provides an ideal approach for one-pot self-construction of assemblies, offering alternatives to LbL and electropolymerization processes with unprecedented functionalization abilities as demonstrated by the *SEEC* approach. Since the Cu(I) catalyst can be easily confined, electroclick possesses great potential for surface patterning and gradient engineering although, to date, improving the resolution of surface patterning has not been a priority. Surprisingly, very few examples of selective patterning on polymer platforms have been reported. However, their development with electroclick would give access to complex films and membranes of great versatility. Testing *SEEC* and morphogen-driven self-construction strategies in patterning mode could fill this void and open the route toward multidimensional patterns and gradients.

3 General Conclusion

The nanoarchitectonic approach, applied to LbL and electroactive systems, gives access to a near infinite number of building block combinations for the design of next generation electrochemical devices. This fast emerging field is anticipated to influence our everyday lives: health monitoring thanks to versatile biosensors and electro-releasable platforms, energy production by designing new supercapacitors and water-splitting devices, or flexible screens based on electrochromic polymers. However, several fundamental questions ranging from ionic conductivities in such films to the assembly driving forces still need to be addressed. Recently, electrochemistry has also been considered as a synthesis tool, and has led to the discovery of electroclick, carbazole electrocoupling (ECC-LbL), and other electroreticulation processes. These new approaches significantly improved the covalent versatility of surface platforms and gave access to novel film architectures such as “mono-polyelectrolyte” coatings. Since the electrochemical stimulus locally induces film deposition, electroclick and carbazole electrocoupling are ideal tools for achieving gradient and patterned surfaces. Applications in fields including biomaterials, electrocatalysis and opto-electronic devices are envisaged.

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