Layer-by-layer assembly of polymeric complexes for electrochromic applications

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NANYANG
TECHNOLOGICAL
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**LAYER-BY-LAYER ASSEMBLY OF POLYMERIC
COMPLEXES FOR ELECTROCHROMIC APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

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A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of Doctor of
Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Abstract

Layer-by-Layer (LbL) self-assembly has been proven to be a very facile and versatile method for thin film fabrication with precise control of the film components and structures. This technique possesses great advantage on integrating materials with different functionalities into a film with designed structures. These features enable LbL self-assembly technique to be a suitable platform for electrochemical applications, which usually require integration of multiple functional components and regulation of interface properties. Conventional polymer LbL films adopt individual polymers as building blocks. However, these films suffer from slow deposition process with only limited amount of materials could be deposited onto the substrate within a deposition cycle. Moreover, LbL films fabricated from individual polymers usually demonstrate compact structure, which also hinders their application in fabricating thin films of which non-compact configuration is preferred. Due to the basic requirements of LbL technique that the adjacent layer should directly interact with each other, this method possesses inherent drawbacks where multi-interfaces are not favourable. Further exploration and modification of LbL technique is desired for better utilization of this prospected technique on electrochemical applications.

In this thesis, we focus on developing polymeric complexes as building blocks for LbL self-assembly, in order to surmount the drawbacks and broaden the application field of LbL technique. Polymeric complexes (PCs) are supramolecular assemblies built up by nonstoichiometric combination of two components. Compared with free polymers, PCs have several advantages including rich varieties of compositions, relatively large dimensions and diverse structures. Thus introducing PCs into LbL enriches the diversity of LbL films, especially for fast deposition of LbL films with special structures and functionalities. However, there are limited reports on using PCs as building blocks for LbL deposition for electrochemical device applications. Aiming at exploiting the potential and merits of adopting PCs in LbL for electrochemical related studies and applications, this thesis is devoted to develop suitable PCs as building blocks to fabricate LbL films for three typical components in an electrochromic device: the electrochromic active layer, the solid polymer electrolyte (SPE) layer as well as the transparent conducting film (TCF). Based

on the basic mechanism and requirements of these three functional layers, different types of PCs were developed to achieve superior performance.

Polyelectrolyte-polyelectrolyte complexes (PECs) were chosen as building blocks for electrochromic active layer, contributing to a fast growth LbL film with porous structure due to the relative large dimensions and charge accumulation of PECs. The resultant electrochromic active films presented larger colouration modulation as well as fast kinetics compared to conventional LbL films. Polymer- α CD inclusion complexes via host-guest interaction were designed and adopted as building blocks for LbL SPE layer fabrication. Taking merits of the steric effect of polymer- α CD complexes, the resultant LbL films possessed lower glass transition temperature and higher ionic conductivity compared to LbL films made from uncomplexed polymers. Conductive PCs were selected to form capping layer on conducting Ag nanowire network. The LbL overcoated films lowered surface roughness of the metallic network without sacrificing the conductivity of the whole layer. The existence of LbL coating was demonstrated to protect Ag nanowire network from oxidation corrosion during the redox reaction.

In conclusion, adopting PCs as building blocks was demonstrated to be a feasible and effective method to fabricate LbL films for electrochemical device applications, surmounting the drawbacks of conventional LbL technique and delivering superior performance.

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Abbreviations

AFM	Atomic Force Microscopy
CD	Cyclodextrin
EC	Electrochromic
EDS	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
LbL	Layer-by-Layer
MDSC	Modulated Differential Scanning Calorimetry
NMR	Nuclear Magnetic Resonance
NW	Nanowire
PAA	Poly(acrylic acid)
PANI	Polyaniline
PDDA	Poly(diallyldimethylammonium chloride)
PEC	Polyelectrolyte Complex
PEDOT: PSS	Poly(3,4-ethylene-dioxythiophene) - poly(styrene sulfonated)
PEI	Poly(ethylene imine)
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PET	Polyethylene terephthalate
SEI	Secondary Electron Images
SEM	Scanning Electron Microscopy
SPE	Solid Polymer Electrolyte
TCF	Transparent Conducting Films
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
UV-Vis	Ultraviolet Visible Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

Over the past decades, Layer-by-Layer self-assembly technique has made remarkable development on both scientific studies about the assembly mechanism and applications for various kinds of functional films. With the expansion of the application fields, the limitations of traditional LbL deposition that adopts individual polymers as building blocks are revealed gradually. Especially for electrochemical applications, the advantages of adopting LbL technique need to be addressed. The potential of incorporating functional materials as well as constructing demanding structures for electrochemical reactions via LbL self-assembly need to be further demonstrated. Novel approaches to develop building blocks which could meet the requirements of electrochemical applications are highly desired.

1.1 Problem Statement

The foundation of Layer-by-Layer (LbL) self-assembly could be dated back to 1960s, when the interaction between polyanions and polycations was investigated, and the concept of LbL technique was firstly brought up.[1] However, this concept did not draw much attention until Decher and coworkers demonstrated multilayer polyelectrolyte films fabricated by LbL self-assembly via electrostatic interaction in 1990s.[2] After that, dramatic development has been made on LbL technique. Due to the high diversity of building blocks as well as the facile process, it has been demonstrated to be one of the most versatile methods to fabricate functional films with control of the components and architectures.

The applications of LbL technique range from ultrathin films for scientific studies to scalable films on arbitrary substrates for various functional devices applications. Considering the unprecedented wide range of functional building blocks and precise control of film structure at molecular level, it is facile to introduce electrochemical active species into a thin film via LbL self-assembly technique. Moreover, LbL technique provides the feasibility to further regulate the charge transfer behavior by controlling the building blocks and the film structure. Thus LbL technique provides a suitable platform for electrochemical studies. With the development and expansion of its application fields, some of the intrinsic drawbacks of traditional LbL deposition which adopts individual polymers as building blocks surfaced. For LbL films which are used in electrochemical devices studies and applications, there are three main issues.

First of all, even though the process of LbL deposition can be simplified to multiple dipping and washing steps, very limited amount of materials could be deposited onto the substrate in each deposition cycle.[3] Under most cases, the electrochemical performance of a film is directly related to the amount of active materials inside the film, that is to say, certain amount of active materials inside the multilayer films is required to achieve satisfactory performance. Thus applying this technique on electrochemical studies is criticized for the time-consuming process—tens or even hundreds of layers need to be stacked together to obtain sufficient amount of active materials, which may cost hours or even days. How to effectively include active materials into LbL films still remains a challenge.

Secondly, polymeric films made by traditional LbL deposition, in which individual polymers are used as building blocks, usually possess compact structures. Due to the high mobility of individual polymers in solutions, the polymers tend to self-adjust their conformation when they adsorb onto the substrate surface and interact with the surface layer, resulting in a conformal and compact film. This compact structure will block the diffusion of the electrolyte into the inner layers when the thickness of the film reaches certain level, thus it is not beneficial to electrochemical reaction.[4] Studies showed that for electrochromic active film, the optical modulation of the film would not kept increasing when the deposition cycles was further increased. On the contrary, the optical modulation stayed similar or even dropped. It was because the electrolyte could not diffuse into the inner layers of the film, thus limited amount of electrochromic active materials could contribute to the performance.[5] During the past decades, many efforts have been devoted to developing porous polymeric LbL films. However, most of the work involves complicated methods, such as incorporating templates, adopting post treatments or synthesizing of polymers with special structures. To develop a facile approach to fabricate LbL films with porous structure, which could promote the electrochemical reaction of the films, is highly desirable.

Third, building blocks with multi-functions that could directly improve certain properties of the LbL films are desired in electrochemical studies or applications. For example, to fabricate a multilayer film as solid polymer electrolyte (SPE), building blocks should be able to form a steady LbL film, at the same time, possess high ability to hold the ions inside the films and promote the transportation of those ions. Individual polymers can barely realize these multi-functions. Even though we can introduce different building blocks with different functions into one LbL film, the configuration of the film will be complicated and the choices of the functional polymers will be limited by whether they could form a stable multilayer film together. Take the SPE as an example, polymers that are promising SPE candidates, such as PEO, PMMA and PVDF, only help to dissolve and host the ions in the matrix.[6] The transportation of the ions inside these matrix are limited by the mobility of polymer segments. Thus to develop a multi-functional building block that can host the ions and at the same time directly contribute to the ion transportation will be favorable for LbL SPE fabrication. The development of multi-functional building blocks is not only beneficial to SPE, but also promote the application of LbL technique on the fabrication of other functional films.

In summary, in order to apply LbL self-assembly on electrochemical related studies and applications, the three main issues are to shorten the deposition process, to construct LbL film with special structures and to develop multi-functional building blocks.

1.2 Objectives and Scope

This thesis aims at exploring and developing polymeric complexes as building blocks for LbL self-assembly. In order to demonstrate the feasibility and flexibility of this approach, we are targeting at fabricating LbL films for the three typical components in a specific type of electrochemical device (the electrochromic device), that is constructed by the electrochromic active layer, the solid polymer electrolyte layer and the transparent conducting layer. Considering different layer has different requirements on the structure and functionality of the LbL films, we will focus on developing optimum polymeric complexes for different functions, realizing the functionalities and improving the performance accordingly.

1.2.1 Develop polyelectrolyte complexes for fast growth LbL films as electrochromic active layer

Electrochromic active layer is the core component of an electrochromic device. This layer functions by changing its optical properties reversibly under certain voltages. The mechanism is based on the redox reaction of the electrochromic materials. Traditional LbL electrochromic active layers, which are constructed from individual polymers, usually suffer from compact structures, are not favorable for the redox reaction. What is more, the electrochromic active layers require substantial amount of active materials within the films to achieve desirable optical modulation. However, during LbL self-assembly, only limited amount of active material could be deposited onto the substrate in each deposition cycle. To a great extent, the slow process of LbL technique hinders its application on electrochromic layers fabrication.

Polyelectrolyte-polyelectrolyte complexes (PECs), consisting of two oppositely charged polyelectrolytes, possess large dimensions and charge accumulation. PECs are promising

candidates for fast growth LbL films with porous structures.[3, 7] The introduction of complexes also provide more opportunity to moderate the charge transfer behavior inside the film during electrochemical reaction. However, their applications on electrochemical active LbL layers are rarely reported, and the merits of polyelectrolyte complexes in the electrochemical reaction have not been illustrated. We hypothesized that carefully designed PECs could be used as building blocks for fast growth LbL films with enhanced electrochromism.

1.2.2 Develop suitable polymeric complexes as building blocks for solid polymer electrolyte fabrication

Electrochemical reactions of materials are usually accompanied by the insertion/desertion or absorption/desorption of ions. These ions are hosted and transported in the electrolyte. Thus electrolyte layer is an essential part of an electrochemical device. However, the ionic conductivity of SPE is relatively low, especially when the temperature is lower than the glass transition temperature of the polymer host, which limits the application of SPE.

Effective ways to improve the ionic conductivity of SPE include reducing the crystallinity of the polymer matrix, improving the mobility of the chain segments of the polymer host, and introducing direct paths for ion transportation into the host. In the LbL films formed by individual polymers as building blocks, the adjacent layers strongly interact with each other, thus the mobility of polymer segments is relatively low. What's more, rarely individual polymer could serve as ions host and at the same time, provides pathway for the ions. Polymeric complexes containing α CD that have special structures and could form ionic pathway are promising substitutions. It is hypothesized that with careful design and control, polymer- α CD complexes could be outstanding candidates for LbL SPE with high ionic conductivity.

1.2.3 Develop transparent conducting films with improved stability via LbL deposition of polymeric complexes as capping layer

Ag nanowire (Ag NW) networks could present high electrical conductivity and good transparency in visible wavelength region, thus they are considered as promising replacement of inorganic based

transparent conducting electrodes. The superior flexibility also enables Ag NW to form conducting layer on flexible substrates, such as polyethylene terephthalate (PET) films. However, the surface roughness of the Ag NW network is very high and the electrochemical stability of the film is poor. In our study, conducting polymeric complexes are chosen as building blocks to fabricate LbL capping layer on Ag NW network to deliver a smooth surface, at the same time, without sacrificing the conductivity and transparency of the film. The conducting polymeric complexes are also expected to act as passivation layer to protect Ag NW from oxidation and corrosion, contributing to a transparent conducting layer with improved electrochemical stability.

1.3 Dissertation Overview

This thesis focuses on addressing the utilization of proper polymeric complexes for LbL films with improved functionality for electrochemical device applications. The LbL self-assembly has been proved to be a very facile and powerful thin film deposition method. However, this technique has been criticized for its time-consuming process and limited control on the structure of polymeric films. Unlike traditional LbL building blocks, which are individual polymers, polymeric complexes possess high flexibility of regulation on their components and structures. LbL films using polymeric complexes as building blocks for three typical components of the electrochromic device are explored. Polyelectrolyte-polyelectrolyte complexes with large dimensions and charge accumulation were used as building blocks for construction of electrochromic active layer with fast growth behavior and porous structure. Polymer-supramolecular complexes with special configuration were introduced and investigated as building blocks for LbL SPE layers.

Chapter 1 presents the challenges and problems existing in the LbL deposition for electrochemical devices applications. The objective and scope of this thesis are discussed, focusing on exploring the design and employment of polymeric complexes as building blocks for LbL films with enhanced electrochemical functionalities. The hypothesis of the work is framed in this chapter.

Chapter 2 presents review on the approaches and progresses on the LbL self-assembly technique and its application on electrochemical devices. The basics of LbL technique is firstly reviewed. Then the features of polymeric complexes and the advantages of using polymeric complexes as

building blocks are discussed. After that, the application of LbL technique on electrochemically functional films, which involves electrochromic active layers, solid polymer electrolyte layers and transparent conductive layers, are reviewed, followed by the discussion of remained challenges.

Chapter 3 presents rationales for the material selection to fabricate the electrochromic active layer, the solid polymeric electrolyte layer and the transparent conductive layer via LbL self-assembly. The designs and synthesis of different kinds of polymeric complexes are introduced. The methods to fabricate LbL films using polymeric complexes as building blocks are described, and the characterization methods for the morphology, optical and electrochemical properties of the resultant films are introduced. Finally, the device structures of testing cells for the LbL films are illustrated.

Chapter 4 presents the development of LbL films with enhanced electrochromism by using PECs as building blocks. PECs with relatively large dimensions and charge accumulation were designed and formed in a facile way, and the surface charge of the complexes could be controlled. At first, LbL multilayer films with dual polyelectrolyte complexes as building blocks, [PSS-PANI/PEI-PSS]_n, were explored. This system was further modified as mono complex system due to its poor electrochemical behavior. After modification, porous structured multilayer film [PANI/PSS-PEI]_n showed fast growth behavior, as well as moderate electrochemical properties. To further improve the electrochromic properties of the film, PAA-PEI complexes, with both PAA and PEI as proton carriers, were adopted instead of PSS-PEI. Systematic characterization on the growth behavior, morphology and electrochemical performance of [PANI/PAA-PEI]_n are conducted and analyzed to illustrate the benefits of using PECs instead of individual polymers as building blocks.

Chapter 5 presents the exploration of supramolecular complexes as building blocks for fabricating SPE layers with high ionic conductivity. Firstly the feasibility of using sphere-like polymeric complexes as building blocks for SPE fabrication is discussed. Then α -cyclodextrin (α CD), a cyclic oligosaccharide that could provide ion transportation pathway, is introduced into LbL film in the form of PEG- α CD supramolecular complexes. The merits and contributions of the PEG- α CD complexes are investigated from the aspects of complexes formation, film growth behavior, thermal and electrical properties of the PEG- α CD/PAA films. Compared with [PEG/PAA]_n films, the LbL films with α CD showed higher ionic conductivity and high water retention ability.

Chapter 6 presents our study on LbL TCF fabrication. Ag NW based TCFs were fabricated via roll-coating assisted LbL technique. Conducting polymeric complexes PEDOT: PSS were adopted as building blocks for LbL capping layer on the LbL Ag NW networks. The PEDOT: PSS/PDDA LbL capping layer contributed to improved conductivity as well as reduced the surface roughness. The capping layer also helped to prevent oxidization and corrosion of Ag NWs. Surface topography, specular transmittance, sheet resistance and stability under ambient condition and electrochemical test were systematically studied.

Chapter 7 concludes and provides reflections on the approaches which are developed to fabricate three basic components in an electrochromic device by LbL self-assembly using polymeric complexes as building blocks. Suggestions on the future works in full device made by LbL technique are provided.

1.4 Findings and Outcomes

This thesis is devoted to exploit suitable polymeric complexes as building blocks for LbL deposition for three typical components in an electrochemical device. Our research leads to several novel outcomes:

1. Using PECs as building blocks is demonstrated to be an effective approach to fabricate fast growth LbL films with porous structure. With careful design of the PEC candidates, PECs could lead to a fast growth film, at the same time facilitate the electrochemical reaction and contribute to enhanced electrochemical properties. It is the first time that PECs are adopted as building blocks for LbL electrochemical layer. This novel approach surmounts the drawbacks of traditional LbL using individual polymers as building blocks on electrochemical studies.
2. Supramolecular complexes have been successfully introduced into LbL films for SPE application. By preforming polymeric complexes, supramolecules formed by polymer and α CD with specific steric configuration were introduced into LbL films and contributed to the film formation as well as the ions transportation. Our work demonstrates a new strategy to engage

functional supramolecules into LbL films. With careful control, supramolecular complexes is shown to be promising candidates for SPE with high ionic conductivity.

3. LbL depositing conducting polymeric complexes PEDOT: PSS was demonstrated to be superior on fabricating polymeric capping layer on Ag NW based TCFs, contributing to enhanced conductivity without compromising transparency. The Ag NW networks with LbL capping layer presented improved stability under ambient conditions as well as electrochemical test.

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Chapter 2

Literature Review

Layer-by-Layer (LbL) deposition is a convenient and versatile method for thin film fabrication. Apart from the simple wet-chemistry procedure, it also shows great advantages of forming functional films with controlled compositions and structures. The applications of this technology range from thin films for basic scientific research to various kinds of functional devices. In this chapter, the basic mechanism of LbL self-assembly is introduced, and the exploitation of different types of the driving forces and the building blocks are reviewed. After that, the recent progresses of applying LbL on electrochemical related studies and applications are reviewed, followed by the discussion of the challenges.

2.1 Basics of Layer-by-Layer self-assembly

As an important branch of supramolecular chemistry, layer-by-layer (LbL) assembly has been demonstrated to be a convenient and versatile method to fabricate functional films with precise control of chemical composition and architecture on micro and nano scales. Although the basic mechanism of LbL assembly can be dated back to the pioneering work of Iler in 1960s,[1] little attention was paid to this technique until LbL multilayer films were demonstrated by Decher and coworkers in the early 1990s.[2, 3] Since then, tremendous development on LbL technique has taken place, including evolution and progress on design of building blocks, exploration of the mechanism and multifunction integration.[4, 5] Compared with other film fabrication methods, LbL assembly possesses four prominent advantages:

(1) It is a convenient and low-cost wet chemical method, which does not require special apparatus and precise operation. In most cases, the fabrication process of LbL films can be simplified as alternative dipping and washing steps.

(2) It allows various applicable materials as building blocks, and feasible regulation of the film structure. The building blocks of LbL assembly include, but are not limited to, synthetic polymers, block copolymers, polymeric microgels, biomacromolecules, inorganic substance, dendritic molecules, organic components, and complexes of these species.[3, 6-9] Several factors can be used to regulate the structure of the film, including the concentration of the building blocks, pH, ionic strength, and temperature.[3, 8, 9]

(3) It provides possibility to integrate multi-functions into a single film, thus it broadens the range of film applications. The process of LbL deposition can be considered as the connection of a series of interfacial assembly. By carefully designing the constituents, materials with different functions could be integrated into a film.

(4) It is particularly suitable for fabricating films in large area on non-planar surfaces.

2.1.1 Understanding of LbL self-assembly process

LbL self-assembly involves sequential deposition of two building blocks onto the substrate, which interact spontaneously with each other. The most well-known LbL assembly is based on electrostatic interaction. As illustrated in Figure 2.1, a multilayer film can be fabricated by alternatively dipping a charged substrate into aqueous solutions of oppositely charged materials with intermediate steps of rinsing in water. In each dipping step, relatively high concentration of the substance in solution leads to an excess adsorption of the substances, contributing to charge reversal on the surface of the substrate. In each washing step, loosely attached materials are removed. Continuous assembly between positively and negatively charged materials results in layered sequence.

Figure 2.1 A schematic of the typical LbL deposition process.

Fundamentally, polyelectrolytes association is an ion exchange process, where polymer-counterion pairs are replaced by polymer-polymer pairs. The reaction of polyelectrolyte complex formation can be described by the following equation[10]:

It could be noticed that when two strong polyelectrolytes are mixed in a solution, the strong interaction between polyanion and polycation based on stoichiometry will lead to a

polyanion/polycation complex with similar amount of negative and positive charged moieties.[2] However, this stoichiometric interaction will not result in a multilayer deposition. Thus the excess of surface charge and the reversal of the surface charge excess after each deposition step are the key factors for fabricating a multilayer film via LbL self-assembly. The excess of surface charge originates from the nature of the polyelectrolyte and exists due to the entropic reasons.[11] It is pointed out that an exact surface charge compensation during the LbL deposition would lead to less chain configurations than a surface charge overcompensation. The surface charge overcompensation allows formation of polymer loops extending into the solution, which is favourable from the entropic aspect.

The first multilayer film deposited by LbL self-assembly was demonstrated by Decher composing of poly(styrene sulfonate) (PSS) as polyanion and poly(allylamine hydrochloride) (PAH) as polycation.[3] In this classical LbL system, the film thickness grew linearly with the increasing deposition cycles. It was pointed out that under the deposition conditions, each layer was only able to interact with the 3-4 neighbouring layers and the film presented a stratified structure. This growing behaviour was denoted as ‘linear growth behaviour’. The LbL films with linear growth behaviour usually possess stratified structure, and the building blocks in each layer interacted strongly with the neighbouring layers and are very well localized, which means the diffusion of the building blocks inside the film is extremely slow.[12] Thus the composition and the structure of the film could be controlled precisely. It is also possible to incorporate specific building blocks into this kind of film at fine location to achieve certain function.

While most of the LbL films grow linearly with the increasing deposition cycles, some of the building blocks, especially weak polyelectrolytes, allow LbL films growing exponentially (which are denoted as e-LbL) under certain condition.[13, 14] The generally accepted mechanism of e-LbL was proposed by Picart, Lavallo and coworkers as ‘in-and-out’ diffusion of polyelectrolytes during the assembly.[15-17] They used fluorescently labelled poly(L-lysine) (PLL) to study the growth of PLL/hyaluronan (HA) LbL film.[15, 18] It was found that PLL diffused deeply into the interior of the film during the deposition. When the film was exposed in HA solution, not only the PLL at the surface but also those laid in inner layers would diffuse to the outer surface of the film and interact with HA electrostatically, which would lead to a thick complex layer (as shown in

Figure 2.2). Based on other studies about e-LbL, it was concluded that most of the e-LbL films required at least one of the candidate polyelectrolyte to have the ‘in-and-out’ diffusion during the film construction. In a film with linear growth, the thickness of one polyelectrolyte layer is typically several nanometers. While for an exponentially growing LbL (e-LbL) film, one single layer could reach a thickness of hundreds of nanometers. Therefore, e-LbL assembly is a facile way to fabricate thick LbL films. Apart from fast growth behaviour, another feature of the e-LbL films is that they are usually poorly structured and behave as viscous liquids. Building blocks inside e-LbL films are weakly interconnected with neighbouring layers. The diffusion coefficient of the building blocks in e-LbL films could reach 10^{-8} - 10^{-9} $\text{cm}^2 \text{s}^{-1}$, which is 6-7 orders of magnitude higher than the diffusion of building blocks in linearly growing films.[12] Thus in contrast to films with linear growth behaviour, it is very hard to control the composition and structure of e-LbL films, not to mention to locate certain species inside the film. It should be highlighted that the polyelectrolytes can only diffuse through the film within a certain thickness; that is to say, exponential growth based on the ‘in-and-out’ mechanism could only exist in the initial deposition cycles. As the deposition cycles increase, starting from a certain layer the primary part of the film would restructure and then hinder further diffusion of the polyelectrolytes, followed by linear growth behaviour of subsequent layers[17].

Other factors, such as increased roughness may also lead to exponential growth of LbL films, which would be discussed in 2.2.2.

Figure 2.2 Confocal laser scanning microscopy observations of the vertical section of PLL/HA films prepared by e-LbL assembly. (a) (PLL/HA)*19-PLL film that contains two labelled layers, PLL19-FITC

(green fluorescence) and HA19-TR (orange fluorescence). (b) (PLL/HA)*25 film that contains two labelled layers of PLL19-FITC and HA19-TR. These evidence revealed that during the deposition process, PLL could diffuse in and out the whole film while HA could not.[18] Reproduced from Ref. 18 with permission from the National Academy of Science / Proceedings.

Even though the adhesion of the building blocks onto substrates mainly happens during the dipping process, washing and interval drying steps also play important roles on LbL film fabrication. Lvov *et al.* investigated how the drying and washing affected the LbL film quality using a quartz crystal microbalance (QCM). They found out that drying at each step increased the thickness of absorbed films because of enhanced surface roughness by drying, which indicated that drying is not favourable for preparing smooth films. On the other hand, immediate water washing between each dipping step was essential for successful alternative adsorption due to removal of loosely attached part.[19]

Other factors, such as counter ions of polyelectrolytes, ionic strength and pH of the solutions will affect the film growth as well. Salomäki and coworkers studied highly charged polyelectrolytes system PSS/PDDA and the corresponding dry LbL films.[20] They found that the thickness of the thin film followed well the position of counteranion in the Hofmeister series. The Hofmeister goes as follows:[21]

The anions on the left of chloride in the series are chaotropic and show weaker interactions with water than water itself, while the anions on the right of chloride are kosmotropic and exhibit strong interactions with water. The chaotropic ions would shield the polyelectrolytes charges during the deposition, resulting in loopy conformation and thick layers. The kosmotropic ions would not shield the charges strongly, allowing the polyelectrolytes to be deposited in a more planar form, which results in thin films. It became more complex when the weak polyelectrolytes acted as the building blocks in LbL deposition, as pH must be taken into consideration. Varying the pH of the weak polyelectrolyte solutions would affect the relative amount of charge on the backbone, thus the conformation of the polyelectrolytes and surface charge density would be changed. By carefully tuning pH conditions of the weak polyelectrolytes, thickness of each single layer and surface properties of the films would be significantly altered. The study on PAA/PAH system, in which the degree of ionization of the two weak polyelectrolytes highly depends on the pH of the

solution, showed that the film thickness would change dramatically within a narrow pH range.[22] In some cases, the films were so thick that the surface charge reflected the dominance of the top polyelectrolyte, different from a surface with mixture of two building blocks in thin films.[23]

Sukhishvili *et al.* summarized the effects of a number of deposition conditions on the formation and the stability of the multilayers, including the type of the interacting polyelectrolyte chains, the ionic strength and the pH of deposition solutions.[24] Those parameters are closely related to the existing forms of polyelectrolytes in the water, which indicates that the trends observed on the multilayers directly reflect the properties of polyelectrolytes in the solutions. Kotov illustrated the contribution of hydrophobic interactions in the LbL deposition by introducing the free energy, of which several independent contributions, including the release of small counterions, partial removal of the hydration shell around oppositely charged polyelectrolytes and the formation of the polyelectrolyte complex, were taken into consideration.[25] His research suggested that without the effects of hydrophobic interactions at the surface, typical polyion systems would not adsorb at all. By using highly sensitive analysis such as isothermal calorimetry titration, Schlenoff and coworkers pointed out that polyelectrolyte association was driven largely by entropy, that is, by the release of counterions and hydrated water from dissolved polyelectrolyte.[26] They also revealed that the polymer segment-surface interactions and the hydrophobicity of the polymer counterions affected the layer thickness and other features of the films significantly. This entropy-driven theory had been further proved by the study of polyelectrolyte complex formation between PSS and PAH under different ionic strengths.[27]

Although LbL assembly only involves simple steps and lots of efforts have been adopted to study the film formation, the assembling mechanism is very complex and still need to be further explored.

2.1.2 LbL self-assembly LbL self-assembly with enriched components and multiple driving forces

The driving force of the LbL assembly is not limited to electrostatic interactions. LbL films assembly driven by hydrogen bonding was firstly investigated by Stockton and Rubner, and Zhang et al. independently in 1997.[28, 29] The major advantage of hydrogen bond driven LbL self-assembly is that the organic solvent could be introduced, thus the species of building blocks for LbL are widely broadened. Stockton and Rubner established the non-electrostatic interaction LbL system of PANI and a series of non-ionic polymers.[28] They found out that molecular weight of the non-ionic polymers and the pH of the solutions played distinct roles on film thickness. For example, in the PANI/PVA system, lowering the pH would promote the growth of film thickness. While in PANI/PVPON system, the film thickness grew with the increase of molecular weight of PVPON, due to the high segmental density of loops and tails of high molecular weight PVPON chains. Considering PANI is also a common candidate in electrostatic interaction driven LbL system, the researchers compared the hydrogen bonded PANI LbL films with PANI involved LbL films driven by electrostatic interaction. They found out that in hydrogen bond driven films, the adsorption of PANI in each deposition cycle was higher than that in electrostatic interaction driven films. Almost at the same time, X. Zhang and his co-workers reported their research on LbL films composed of two typical hydrogen bonding complementary partners, which are PAA as hydrogen bond donor and PVPON as hydrogen bond acceptor.[29] The formation of the LbL films, the interaction between the two polymers and the morphology of the films were systematically characterized by UV-vis, XRD, FTIR and AFM measurement. In their later study of PVPON/DEN-COOH system, post-treatment was applied to obtain a microporous LbL film.[30] Sukhishvili and Granick further investigated the effect of deposition environment on the construction of hydrogen bond driven LbL films.[31, 32] It is known that compared with electrostatic interaction, hydrogen bonding is a relatively weak interaction. Thus the hydrogen bonded LbL films are very sensitive to the deposition conditions. The films could be destroyed by changing pH, temperature, ionic strength, and even external stresses or electrical field. A very classical case is about the stability of PMMA/PVPON multilayer films under different pH. It was found that the PMMA/PVPON LbL films could stay stable up to pH=6.9. After that critical pH, the ionization degree of carboxyl groups of PMMA was high enough to cause strong electrostatic repulsion between PMMA chains, which could lead to the collapse of the hydrogen bond driven film. Simultaneously, with the increasing ionization degree of PMMA, the hydrogen bond between PMMA and PVPON was weakened. Thus after being exposed to environment with pH higher than

6.9, the films began to decompose.[32] On one hand, the high sensitivity to the environment limits the fabrication condition of hydrogen bond driven LbL films; on the hand, it also enables the establishment of erasable polymeric multilayer systems. Inspired by the pH-sensitive LbL system, the pH deformable multilayer capsule assembled by hydrogen bonding was developed and used for drug/therapeutic delivery and bioreactors.[33, 34]

There are some special components that would act as both donor and acceptor, resulting in highly ordered arrangement of molecules in the film. Huo et al. demonstrated hydrogen bonding LbL system by alternatively stacking the same building block.[35] A dendrimer with carboxyl groups on its periphery, which could serve as both hydrogen donor and acceptor, was chosen for the self-deposited LbL film. It was also found that this specific self-deposited film could only exist under certain pH range. The film would decompose in solutions with $\text{pH} < 5$ or $\text{pH} > 9$, which further proved the hydrogen bonding between dendrimers was the dominating factor of this LbL film construction. Marks and co-workers designed a special molecule which formed layered structure through intermolecular triple hydrogen-bonding interactions.[36, 37] The film was constructed by molecules aligned head-to-tail under vapour phase and preferentially perpendicular to the substrate (see Figure 2.3). The molecules inside the film were highly ordered and orientated in certain direction, making it possible to regulate the electro-optic properties of the film. Thus this strategy is very important for electro-optic effect related applications.

Figure 2.3 Formation of multilayer films via intermolecular hydrogen bonding.[36] Reproduced from Ref. 36 with permission from the American Chemical Society.

Besides hydrogen bonding, π - π interaction and covalent bond are also considered as the promising driving force for LbL deposition. Π - π interaction usually acts as the supplementary force of electrostatic interaction or hydrogen bonding that is widely exist in the LbL deposition involving graphene, carbon nanotube and some dye molecules because of their conjugated structure.[38, 39] Covalent bond is used to stabilize the film after being built up, when the components of the film have active sites to form covalent bond. Caruso and co-workers introduced click chemistry into LbL deposition.[40] The film was formed by PAA with either azide and alkyne functionality solutions containing copper sulphate, finally covalently linked film with designed structure could be obtained. Other interactions, including biochemical force, physical force, supramolecular interactions and sol-gel interactions, were also explored as driven force for LbL assembly.[41-44]

With the expansion of driving force, the species of building blocks for LbL self-assembly was also enriched. Besides polymers and small organic molecules, nanoparticles, nanotubes, nanowires and 2D materials were also introduced into LbL films. Caruso et.al used silica nanoparticles as sacrificial template to build up the porous films. They first synthesized PAA stabilized SiO_2 particles, then assembled $(\text{PAA-SiO}_2/\text{PAH})_n$ multiple layers. After cross-linking of the PAA and PAH in the film, SiO_2 particles were dissolved and removed from the film, leading to nanoporous thin films.[45] Liz-Marzan and co-workers reported their systematic study of optical properties of a LbL film fabricated by assembling polyelectrolytes and Au nanowires.[46] Noy and co-workers decorated carbon nanotubes with aromatic pyrene derivative with the help of π - π interaction. These positively charged modified carbon nanotubes were used to assemble with proper polyanion through LbL method, resulting in a conductive nanowires network with an insulated coat.[47] Paul and co-workers studied ultra-strong $(\text{PDDA}/\text{MTM})_n$ multilayer films, which showed higher strength and higher Young's modulus when compared with traditional polymer films.[48] Graphite oxide was also used as complementary partner of PAH and PANI to construct LbL films. By carefully controlling the pH of the adsorbing solution, Gorchinskiy and co-workers successfully achieved continuous GO/PAH and GO/PANI film.[49] Surface morphology studied by AFM revealed that the flexible GO sheets easily folded and overlapped with each other when adsorbed onto the previous layer. Preliminary studies on electronic properties of the GO/PAH and GO/PANI films were also conducted. It is found out that the diode like behaviour was maintained in both

films, while the conductivity of the GO/PANI LbL films was higher than that of GO/PAH films due to the existence of PANI.

2.1.3 Spin-assisted and Spray assisted LbL film depositions

The establishment of LbL self-assembly and most of the early studies of LbL films relied on the traditional dip-coating method. Each dipping step involves the diffusion of the building block, adsorption onto film surface / desorption from the film surface and rearrangement of the building block on film surface. Normally it will take tens of minutes to deposit a single layer onto the substrate, depending on the deposition conditions and the nature of the building blocks. Thus fabrication of a multilayer film is quite a long process. To accelerate the fabrication of LbL films, spin-assisted and spray-assisted LbL systems were developed as more efficient and commercially feasible methods.

Cho and co-workers first combined LbL self-assembly with spin-coating method and successfully obtained PSS/PAH multilayer films.[50] The PSS/PAH multilayer films were fabricated by alternatively spinning PSS and PAH solutions onto the substrate, with interval washing and drying step. Film thickness could be regulated by the concentration of the polymer solutions and the spin speed. The time of a single layer deposition could be shortened to several seconds. Compared to LbL films fabricated by dip-coating method, the spin-assisted LbL films showed lower surface roughness due to the air shear force during the spinning process.[51] During each deposition cycle, the film fabricated by spin-assisted LbL was thicker than the dip-coating LbL film, indicating more adsorption of polyelectrolytes during each deposition cycle for spin-assisted LbL system. It was attributed to the fast elimination of water during the spinning, which increased the concentration of the polyelectrolyte and promoted the electrostatic interaction between opposite charged building blocks. Because of the existence of air shear force and the short interaction time with building block solutions, the self-adjustment and interpenetration of the building blocks within the film are suppressed. Thus the resultant LbL films usually possess ordered layer structure. Even though the spin-assisted LbL assembly could effectively shorten the time taken for fabricating multilayer films, and could also provide smooth surface with ordered internal structure, to completely replace

dip-coating LbL assembly with spin-assisted LbL technique is restricted by the inherent features of spin-coating, which could not be applied onto nonplanar surface and large area film fabrication.

Figure 2.4 Schematic representation of the process of (a) spin-assisted and (b) spray-assisted LbL self-assembly.[52] Reproduced from Ref. 52 with permission from the Royal Society of Chemistry.

Spray-assisted LbL assembly was developed even earlier than spin-assisted LbL technique.[53] Building blocks are alternatively sprayed onto the substrate, with the rinsing step realized by pure water spraying. It shows great advantage on large surface coatings within a short time. Since each spraying step only lasted for several seconds, micro-meter thick LbL films could be deposited within a reasonable time. However, it failed to catch attention in the first years because this technique was applied in a crude manner and large amount of building blocks (could reach 99% of the total amount[54]) were wasted during the spray process. In 2005, Izquierdo and co-workers reported their systematic study of the spray-assisted PSS/PAH LbL film.[55] They investigated the influence of several conditions on the LbL film build-up, which included solution concentration, spraying time, rinsing step and the way the substrates were placed. They found out the less concentrated polyelectrolyte used would determine the film thickness. The rinsing step could be omitted in order to obtain thicker films compared to dipping LbL, at the same time the film quality was maintained. Further study about the film structure and film growth behaviour of PSS/PAH by Felix et al. showed that compared to dipping LbL films, spray-assisted LbL films were more stratified and possessed smooth surface.[56] These features of spray-assisted LbL films are similar to spin-assisted LbL films. After that, much effort has been spent on spray-assisted LbL assembly. Polymeric multilayer films, polyelectrolyte/nanoparticles films, polyelectrolyte/micro-molecules films and inorganic/inorganic multilayers have been successfully fabricated by this technique.[53] Spray-assisted LbL assembly is not only suitable for film fabrication on planar

substrates, but also capable of multilayer coatings on non-planar substrates. For example, Hammond and her group demonstrated multilayer coatings on electrospun fibers membrane using spray-assisted LbL assembly.[57] They pointed out that suitable pressure gradients across the membrane was the key factor to obtain a conformal coating on the fibers. Instead of a conformal coating under low vacuum, high vacuum led to limited coverage of the coating through the whole membrane, while absence of vacuum resulted in bulky deposition on the surface of the membrane. Even though in most cases, spray-assisted LbL film is thinner than the dipping LbL film under the same deposition cycle, which is due to the limited time for the surface interaction and the compressing force from the spraying process, each spraying step only lasted for several seconds. Thus micro-meter thick LbL films could be deposited within a reasonable time. However, traditional dipping LbL technique still holds the priority of depositing conformal coatings on arbitrary substrates.

2.2 Polymeric Complexes as building blocks

As discussed before, LbL self-assembly is based on nonstoichiometric interaction between two components. The building blocks alternatively adsorb onto the substrate surface and further form a multilayer film. With the similar mechanism, polymeric complexes (PCs) are formed by nonstoichiometric combination of two candidates when directly mixed together. By carefully controlling the formation conditions, stable PC could be obtained and further used as building blocks for LbL self-assembly. Considering the diverse candidates and special spatial structure of the PC, introducing PC as building blocks presents more possibilities on fabricating LbL films with particular functions or structures.

2.2.1 Formation of polymeric complexes

Polymeric complexes (PCs) represent a large variety of supramolecular assemblies held together by multiple weak interactions, including polyelectrolyte-polyelectrolyte complexes (PECs), polyelectrolyte-surfactant complexes, uncharged polymer-polymer complexes and polymer-inorganic hybrid complexes.[52] Polymer-inorganic hybrid complexes are commonly adopted as a facile method to stabilize inorganic materials. Due to the rigid nature of inorganic materials, the

hybrid complexes will exhibit mostly the features of inorganic materials, and the modulation of structures and functionalities on these hybrid complexes and the consequent LbL films is highly confined. Considering these factors, the polymeric complexes or PCs discussed in this thesis DO NOT include polymer-inorganic polymer complexes. The PCs are usually built up by nonstoichiometric combination of two components, resulting in an abundance of uncoordinated groups on the outer surface of PCs.[58] These groups make PCs suitable for LbL assembly with complementary partner species to produce composite films. Two models of PC structures have been adopted in the literature: one is the ladder-like structure, where the complex formation is on a molecular level via conformational adaptation; the other one is scrambled-egg model, where a high number of chains are incorporated into a particle. Due to the special steric effect, particle-like PCs are more attractive when being introduced into LbL assembly. It is worth noting that the PCs are so called “living system”, and very sensitive to the environment. Thus the structure and the configuration of the PCs could be tailored by tuning the parameters, such as molecular weight of the polymer, chain mobility and charge density of the polymer chain, mixing ratio of the PC candidates, solution pH, ionic strength and temperature, before or after the formation of PCs[59]. Compared with free polymers, PCs have several advantages including rich varieties of compositions, relatively large dimensions and diverse structures. Thus introducing PCs into LbL enriches the diversity of LbL films, especially on fast deposition of LbL films with special structures.

Figure 2.5 Illustration of different types of polymeric complexes. (a) Polyelectrolyte complexes; (b) uncharged polymer-polymer complexes; (c) polyelectrolyte-surfactant complexes; (d) polymer-inorganic complexes.[52] Reproduced from Ref. 52 with permission from the Royal Society of Chemistry.

2.2.2 Features of LbL films with PC as building blocks

The large dimensions of PCs promote rapid fabrication of polymeric films by LbL assembly. In 2002, Caruso and co-worker first demonstrated that nonstoichiometric polyelectrolyte-polyelectrolyte complexes (PECs) could be used in LbL multilayer deposition with another polyelectrolyte.[60] By tuning the ratio between PDDA and PSS, they successfully obtained stable positively charged PDDA-PSS complex and negatively charged PSS-PDDA complex. PDDA-PSS/PSS and PDDA/PSS-PDDA multilayer films were prepared, and the growth behaviour and the morphology of the films were characterized by QCM and UV-Vis spectrometer, and AFM, respectively. They found out that compared to LbL films with uncomplexed polyelectrolytes, the films containing PECs showed larger mass change during each deposition. Soon after that, Müller and co-workers reported their research on the effects of pH, polyanions, surface modification of the substrates, as well as the configuration of PECs on the adsorption behaviour of PECs.[61] But none of these pioneer works illustrated the advantage of using PCs as building blocks for LbL deposition. Sun and co-workers focused on rapid deposition of LbL films using PCs.[62] They systematically studied and demonstrated the rapid growth and tailored the structures of LbL films built up by polymeric complexes. Negatively charged complex of PAA and diazoresin (DAR), and positively charged complex of DAR and PSS were used to fabricate fast growing LbL film.[63] The (PAA-DAR/DAR-PSS)₂₀ films had an average thickness of $2.69 \pm 0.15 \mu\text{m}$. As a comparison, the thickness of (DAR/PAA)₂₀ and (DAR/PSS)₂₀ films prepared under the similar condition were only around 40 nm, which were much thinner than the films fabricated by complexes. PCs formed by hydrogen bonding were also investigated for LbL assembly. Hydrogen-bonded PVPON-PAA complex and poly(methacrylic acid) (PMAA) were deposited alternatively on the substrate by hydrogen-bonding interaction, resulting in a (PVPON-PAA/PMAA)₃₀ film with a thickness of $1.5 \mu\text{m}$. [64] It is worth noting that the PVPON-PAA/PMAA film exhibited exponential growth because the surface roughness of the film increased with the increasing number of deposition, which provided larger surface area and allowed more building blocks to deposit on the film in the following deposition cycles.[63] Similarly, the fast growing film (PAA-(Py@CTAB)/PDDA) benefited from the large dimension of polymeric complex PAA-(Py@CTAB), which is composed of surfactant micelle stabilized uncharged species pyrene (Py), as well as from the increase of surface roughness with increasing deposition cycles.[65]

Figure 2.6 Illustration of fast growing $[\text{PVPON-PAA/PMAA}]_{30}$ LbL film using PVPON-PAA complexes and PMAA as building blocks, compared with traditional LbL film $[\text{PVPON/PMAA}]_{30}$ which was constructed from individual polymers PVPON and PMAA.[64] Reproduced from Ref. 64 with permission from the Royal Society of Chemistry.

Besides fast growth behaviour, using PCs as building blocks could also achieve multilayer films with porous structure. Generally speaking, porous polyelectrolyte films prepared by LbL deposition require phase separation or the assistance of special templates, because uncomplexed polyelectrolytes are flexible in the aqueous solution and have a strong tendency to self-adjust their configuration to form a smooth and flat film during the deposition process. However, electrostatically cross-linked PECs are more rigid than their corresponding free polyelectrolytes, thus making them good candidates for building up porous films. Sun and coworkers systemically studied the effect of ionic strength to the morphology of PSS/PAA-PAH multilayer films.[66] The polymeric complex PAA-PAH possesses a hydrophobic core structure with a hydrophilic shell. They found out that by adding NaCl to the PAA-PAH system, the size of hydrophobic core would grow. Hydrophobic-hydrophobic interaction between the complexes induced micro phase separation during the deposition, thus a non-compact film was formed. Upon drying the film with N_2 at the last deposition layer, a dewetting-induced porous film was obtained. Polymeric films with microporous structure could also be obtained by carefully tuning the ratios between the two components in the PECs used in LbL deposition. In the PAA/DAR-PAA multilayer system, the researchers found out that when the ratio of DAR: PAA was changed from 1: 0.4 to 1: 0.1, the resultant films showed different morphologies. For the films fabricated from the DAR-PAA complexes with higher DAR: PAA ratio, due to the existence of relatively free DAR, the films were continuous with a relatively smooth surface. For the films fabricated from the DAR-PAA

complexes with lower DAR: PAA ratio, the films showed hierarchical structure with microporous surface, because of the more rigid DAR-PAA complexes and the loosely packing of those complexes.

Figure 2.7 Micro-porous LbL films fabricated from PAH-PAA complexes and PSS via LbL self-assembly with the existence of high concentration NaCl.[66] Reproduced from Ref. 66 with permission from the American Chemical Society.

In summary, compare with uncomplexed polyelectrolytes, PCs possess relatively large dimensions and more rigid structures, which makes them good candidates for fast growth LbL films fabrication. The relatively large amount of charges carried by PCs also cause repulsion in-between, resulting in loosely packed structure during LbL deposition. By carefully tuning the deposition conditions to further control the configuration of the PCs, porous LbL films could be obtained without any template or complicated post-treatment method. Moreover, using PCs as building blocks also facilitate the incorporation of functional species. In principle, compatible complementary building blocks are required when using uncomplexed functional species for LbL assembly. If the functional species are involved in the complexed form, the complementary parts for LbL film could be found based on the other candidate in the complex. Hence, there is more possibility to incorporate the functional species into LbL films successfully. However, there is very little research on this field.

2.3 LbL technique used in electrochemical studies

LbL self-assembly as a thin film fabrication method, not only embodies its value in providing a new platform to study the interaction between different building blocks and the properties of the

resultant films, but also shows its facileness and superiority on fabricating functional films towards various applications. In general, an electrochemical device consists of 3 main parts: the electroactive layer, the electrolyte layer and the electro-conductive layer. The following section of this review will focus on the application of LbL technology on these three parts of an electrochemical device.

2.3.1 Electrochromic LbL films

Electrochromic (EC) materials are able to change colours reversibly under certain applied potentials. The mechanism relies on the change of the electronic states, especially π - or d- states, of the active materials during the redox reaction. For EC materials, this change of electronic states is usually associated with distinguishable change in the absorption or reflection spectra.[67] Different from light emitting diodes (LED), which is based on active emissive mechanism, the EC materials require only an initial current pulse at a certain potential that is strong enough to induce the desired electrochemical reaction and color change. This change of color is permanent and the EC device only demands backlighting.[68, 69] The low energy consumption, large optical modulation and stable memory effect make EC devices popular and promising candidates for various applications, such as dynamic windows, panel displays and smart papers.

LbL self-assembly has been successfully applied on EC film fabrication since 1997.[70, 71] Generally speaking, there are two types of LbL EC films: one is pure organic films based on conjugated polymers; the other one is organic-inorganic films with inorganic EC active materials. Most of these films are driven by the electrostatic interaction between different building blocks, while there are several studies reporting LbL EC films based on coordinative interactions to achieve metallopolymer networks.[72-74] Two main parameters are used to compare the performance of EC films: optical modulation (the absorbance or transmittance change at certain wavelength when a potential is applied, which is denoted as ΔA or ΔT) and switching time (define as the time required to reach 90% of the color change).

For LbL EC films with conjugated polymers as active materials, the variation in the color comes from the doping/de-doping of the conjugated polymers during the redox reaction, accompanied by the transportation of electrons and ions.[67] Polyviologen (PV) is the first EC active polymer

explored in LbL EC film fabrication. In 1997, Schlenoff and co-worker fabricated a LbL film with positively charged PV and negatively charged PSS as building blocks.[70, 71] Due to the interpenetration of PV and PSS layers, the PV in the film was electrochemically accessible. The color of the film changed corresponding to the change of the voltage applied. This is the first demonstration of LbL EC film. After that, Hammond and her group successfully fabricated a fully functional EC device, which consisted of a PAMS/PANI multilayer film on ITO-coated glass and a PEDOT:PSS/PEI multilayer film on ITO-coated glass as anodic and cathodic working electrodes, respectively, with a PMMA based gel electrolyte as the ion conductor.[75] This EC device showed maximum optical contrast of $\Delta T=30\%$ at 640 nm within 1 s. They further improved the optical modulation by replacing PANI with poly(hexylviologen) and the optical contrast was increased to $\Delta T=82\%$.[76] This is still one of the highest optical modulation recorded from full polymeric EC LbL device. Heflin and co-workers used sulfonic acid doped PANI (PASA) as polyanion and PANI as polycation to prepare PASA/PANI multilayer films.[77] In this system, both charge complementary parts are EC active materials. The resultant films showed an optical contrast of $\Delta T \sim 47\%$ at 600 nm for a 30 bilayer film. However, when the number of deposition cycles were further increased, the contrast of the film was not improved much. This was because the compact structure of the film blocked the ionic transportation throughout the film, thus hindered the doping/de-doping process of the inner layers. At the same time, the poor ionic conductivity of the thicker film made difficulties of the redox reaction of the outer layers. Similar phenomenon was also observed in the sulfonate derivative of PEDOT (S-PEDOT)/PAH multilayer EC film, in which the S-PEDOT was the EC active material.[73] Polymerized aniline derivatives and acid doped PANI were also widely studied in LbL EC films. The optical properties and kinetics of these films were affected by the groups modified on aniline or the doping acid.[77-79]

Figure 2.8 Demonstration of a colored and bleached solid state EC cell.[75] Reproduced from Ref. 75 with permission from the John Wiley and Sons.

Figure 2.9 Transmittance/initial transmittance ($\%T/\%T_0$) when the film was switched from color state to transmittance state. Note that the 50 BL film decreased significantly, indicating limited active materials inside the film could be utilized.[73] Reproduced from Ref. 73 with permission from the John Wiley and Sons.

Organic-inorganic hybrid LbL EC films combine the merits of the two, i.e., the flexibility of polymers and the chemical and thermal stability of inorganic compounds. There are two kinds of hybrid LbL EC films. One is to use EC active inorganic materials, such as tungsten oxide,[80-82] poly(oxometalates),[83-85] and Prussian blue (PB),[86, 87] with charge complementary polymers

to fabricate multilayer films. In a PB/PANI LbL film, with both charge complementary parts as EC active materials, a fast switching time as well as a high contrast can be delivered.[88] The electrochromic properties of this hybrid LbL film were superior to that of pure PB film. In this kind of EC film, the advantages of inorganic EC materials are very well reflected, for example, high coloration modulation, high chemical stability and good cycling retention.[67, 81] The other is to improve the performance of the organic EC materials by introducing inorganic components into the LbL films. Shi and co-workers used reduced graphene oxide and PANI as building blocks.[89] The resultant LbL films showed improved electrical and ionic conductivities, leading to a shorter switching time than that of spin-coated PANI thin film. Lu and co-workers synthesized star-like polyaniline-tethered silsesquioxane (POSS-PANI) nanocage, and fabricated (POSS-PANI/PAMPS)_n and (POSS-PANI/sulfonated-PANI)_n films.[90] The special configuration of POSS provided more accessible doping sites of PANI and promoted ion transportation, thus resulting in higher coloration modulation and improved switching kinetics.

2.3.2 LbL films as solid polymer electrolyte (SPE)

The layer-by-layer deposition technique offers distinctive advantages for the design and development of ionic conductive films that can be used as solid polymer electrolytes. Firstly, most of the LbL polymer films are inherently amorphous solids with mechanical properties superior to those of gels and crystalline solids.[91, 92] The films do not flow or deform easily, but remain flexible. Secondly, LbL polymer films could be processed to be very thin and defect-free, which can lead to thinner solid electrolytes in devices, reducing the inner resistance of the whole device.[93] Thirdly, LbL films can be easily tailored to create surface passivation and incorporate a wide variety of materials to achieve chemical compatibility and high performance.[91, 92]

The ionic conductivity of the polymeric film is described by the relationship:[67]

$$\sigma = \sum_i \rho_i Z_i \mu_i$$

where the sum ionic conductivity involves all the ionic species, ρ_i stands for the number density of type i ion, Z_i represents the charge of type i ion and the μ_i is the mobility of the type i ion.

Durstock and Rubner first investigated the ionic conductivity of [poly(allylamine hydrochloride)/poly(sodium 4-styrenesulfonate)]_n ([PAH/PSS]_n) films and [PAH/PAA]_n films,[94] observing a maximum conductivity of $2 \times 10^{-7} \text{ S cm}^{-1}$ at 90% RH and room temperature, which was too low for most of the electrochemical applications. The ionic conductivity of these films was dependent on assembly conditions, such as ionic strength, and the moisture inside the films. Increasing humidity or temperature will also improve the mobility of the ions inside the film, leading to a higher ionic conductivity. Later studies by Farhat and Schlenoff demonstrated that ion transport in multilayer films could be improved by post-treatment such as immersing the films in additional ions bath.[95]

However, these kind of electrostatic LbL films were concluded as not suitable for ions transfer applications because of the limited ion number and poor ion mobility inside the films. The limited ion number in the film may result from the large extent of polyion pairing and rejection of residual small ions from the LbL bulk films, especially for strong polyion systems. Thus in general, an electrostatic LbL film cannot contain as many as dissociable small counterions as a neat film of either polyion, which could carry one counterion per monomer unit. Besides, the hydrophobic groups of common polyelectrolytes, such as what PAH, PDDA or PSS possess, prevent residual or added salt from dissolving into the film, which also causes limited ion number. The poor ion mobility is usually considered to be from the high cross-link density of the polyelectrolytes. It is believed that ions move by hopping from trap to trap within the multilayer films, thus the mobility of the ions strongly depends on the dynamic of the polymer segments.[96] The constraint small-segment polymer dynamics directly lead to poor ion mobility. What's more, each ion pair within the film could behave as a 'coulomb trap', hindering ions migration by temporary associating with the migrating ions.[97] Thus how to increase the concentration of free ions inside the LbL film and improve the mobility of the polymer segments are the critical points to improve the ionic conductivity of the LbL films.

In order to figure out the problems mentioned above, two possible methods were proposed and explored by Hammond and co-workers. The first design was focused on improving ionic conductivity by maximizing small ion concentration and minimizing cross-link density. They investigated a series of LbL films comprising weak polyelectrolyte LPEI and polyanions.[92] The ionic cross-link density could be modulated by adjusting pH because the protonation degree of

LPEI is highly depended on pH. Ionic conductivity greater than $10^{-5} \text{ S cm}^{-1}$ at 100%RH and room temperature was achieved within [LPEI/PAMPS]₃₀ and [LPEI/PAA]₃₀ films. More exciting results were observed in [PDAC/sPPO]_n films with ionic conductivity of $7.00 \times 10^{-2} \text{ S cm}^{-1}$. [98] Different from introducing weak polyelectrolytes, the strategy used was to decrease ionic cross-link density of the films and to selectively screen charges by adding salt to the sPPO solution. The addition of salt also increased the water uptake of the films, which could further increase the ionic conductivity.

The second design was to explore LbL assembly exploiting non-electrostatic interactions, such as hydrogen bonding, to circumvent the limiting effects caused by electrostatically deposition. PEO is one of the most popular polymer matrixes for solid electrolyte because of its good solubility of lithium salts. [99, 100] However, the ionic conductivity of PEO based solid polyelectrolyte layers was limited by high crystallinity of PEO backbones. As mentioned above, the transportation of lithium ions in PEO matrix relies on the local relaxation and segment motion of the PEO chains, which only can be realized in amorphous phase of PEO. While for PEO with high molecular weights, the formation of amorphous phase usually happens above 60 °C. Thus main efforts were made to decrease the crystallinity of PEO under room temperature to improve the ionic conductivity of PEO based electrolyte. LbL deposition of PEO and complementary polymers via hydrogen bonding interaction is one of the approaches. Delongchamp and coworkers demonstrated the fabrication PEO/PAA LbL multilayer films driven by hydrogen bonding. [6] As PEO possessed good ability to solvate low lattice energy lithium salt, the [PEO/PAA]₁₀ post treated with lithium salt solutions showed ionic conductivity higher than $10^{-4} \text{ S cm}^{-1}$ at 100%RH. Nguyen and co-works fabricated polyelectrolyte films [PEI/PAA/PEO/PAA]_n which combined electrostatic interaction and hydrogen-bonding in the existence of small amount of Li⁺ salt. [91] The film showed an ion conductivity above $10^{-5} \text{ S cm}^{-1}$ at 52%RH. The function of the film was further demonstrated in a working electrochromic device with this multilayer film as electrolyte.

Figure 2.10 A tetralayer design LbL film, combining hydrogen bonding and electrostatic interaction.[91]
Reproduced from Ref. 91 with permission from the American Chemical Society.

2.3.3 LbL technique for transparent conducting films (TCFs) fabrication

Transparent conducting electrodes are widely used in electrical devices, such as smart windows, displays, and touch screens. With the rapid development of flexible and stretchable devices, there is an urgent demand of for conventional transparent conducting electrodes made from conducting inorganic oxides, such as indium doped tin oxide (ITO) and fluorine doped tin oxide (FTO), due to their brittle nature. Among different kinds of conducting materials, carbon materials, such as carbon nanotubes (CNTs) and reduced graphene oxide (rGO), and metallic nanowires are considered as promising TCF candidates of because of their high conductivity, high resistance to flexural fatigue and ease of processing.

The versatility of of LbL technique on multilayer films construction made it a popular approach for fabrication of TCFs based on carbon materials. Hammond and co-workers first demonstrated LbL conducting films by alternatively depositing negatively charged multiwall CNTs and positively charged multiwall CNTs onto a solid substrate (as shown in Figure 2.11).[101] By carefully adjusting the deposition and post treatment conditions, the multilayer film could deliver a conductivity around 10 S/cm, while the transmittance was poor. Similar strategies were also applied on TCFs made from oppositely charged rGO and CNT/rGO hybriide films, of which the best TCF possessed a sheet resistance around 8 k Ω /sq with a transmittance of 81% at 550 nm.[102, 103] The poor conductivity of LbL TCF was attributed to the intrinsic requirement of LbL technique on the surface modification of carbon materials. In order to form a multilayer film via LbL self-assembly, the carbon materials are usually modified with functional groups, such as –

NH_3^+ group and $-\text{COO}^-$ groups, to adopt surface charge. However, this kind of modification method will disrupt the sp^2 bonds of carbon materials and lead to a low conductivity. Surfactants could also be used for surface charge modification, while the surfactant wrapped on the CNT or graphene surface will raise the resistance of the CNT-CNT or graphene-graphene junctions, which dramatically reduce the conductivity of resultant LbL films.[104] Even though much effort has been made to improve the conductivity of carbon based TCFs, LbL technique showed inherent drawbacks on carbon based TCF fabrication.

Figure 2.11 Illustration of LbL deposition of negatively charged multiwall CNT and positively charged multiwall CNT.[101] Reproduced from Ref. 101 with permission from the American Chemical Society.

Metallic nanowires (NW) with a network structure are also widely studied as promising candidate for TCF fabrication because of the superior conductivity of metallic materials and high transparency of the network structure. The group of Lee has successfully demonstrated a Ag NW based TCF fabricated by roll coating assisted LbL technique (Figure 2.12).[105] It was pointed out that the intermediate PDDA layer was not only essential for LbL film formation on the PET substrate, but also could help to neutralize the surface charge of Ag NW (which was contributed by the PVPON surfactant on Ag NW) and reduces the repulsion between Ag NW, leading to better connection between Ag NW and lower sheet resistance of the resultant TCFs. With a graphene oxide overlayer, the TCFs could present a low sheet resistance around $10 \Omega/\text{sq}$ while maintaining a high transparency around 91%.

Figure 2.12 Illustration of roll coating assisted LbL strategy for Ag NW based TCF fabrication.[105] Reproduced from Ref. 105 with permission from the American Chemical Society.

2.4 Challenges in LbL electrochemical films

The LbL self-assembly provides access to diverse combinations of building blocks for various kinds of applications. However, there are still several challenges when this technology is applied on electrochemical devices. First of all, as discussed in 2.1.3, traditional LbL films suffers from slow process ($<20 \text{ nm h}^{-1}$), due to the kinetics of self-assembly and the inherent feature of the multi-layered structure. Especially for electrochemical LbL films, in order to incorporate enough active materials to get satisfactory performance, tens even hundreds of layers are needed to be assembled into a single film, which usually costs a long time.[75-77, 106, 107] To develop a strategy to incorporate large amount of active materials into LbL films within a short time will facilitate the application of the LbL self-assembly on electrochemical applications.

Secondly, carefully design film components and structures are required to ensure optimum electrochemical behaviours in the LbL films. There are different requirements on the deposition strategy for different applications. For example, LbL films fabricated with free polyelectrolytes usually possess compact structure due to the high flexibility and self-adjustment of the polymer chains during the deposition process. However, this kind of compact structure is undesirable for the electrochemical reaction. As discussed in 2.3.1, the optical modulation did not increase continuously with the increasing deposition cycles because the compact structure would hinder the ion transportation to the inner layers and made those layers inaccessible for electrochemical reaction. Thus polymers with specific steric effects or incorporating templates are welcomed to

provide a porous structure to promote electrochemical reaction in LbL films. Nevertheless, incorporating polymers with specific steric properties will take a lot of efforts on molecular design and synthesis, not to mention that there will be a lot of limitations when templates are used, such as the size of the film and the shape of the substrates should be matched with the templates. Thus how to construct LbL film with porous structure in a facile method still remains a challenge. When talking about LbL films used as SPE, the mobility of the ions inside the LbL film is the critical factor. As discussed in 2.3.2, LbL films with strong interaction between adjacent layers suffer from low loading capacity of free ions and restricted mobility of polymer segments. Thus LbL films driven by relatively weak interaction, such as hydrogen bonding, are more suitable for SPE. However, in hydrogen bond driven LbL system, the ionic strength will affect the formation and stability of the LbL film a lot. Taking PEO based LbL films as an example, PEO is known as hydrogen bond acceptor, and one of the most popular polymer matrix for SPE because of the high solubility of lithium ions in PEO matrix. However, there is a competitive effect between the interaction of lithium ions with PEO chain and the hydrogen bonding between PEO and hydrogen bond donor, that is to say, when the loading of lithium ions on PEO is high, the interaction between PEO and the hydrogen bond donor will be weaker, hence impeding the LbL film formation. Thus introducing functional components which can promote ion transportation, and at the same time would not affect the film formation into LbL films is highly desirable.

Third, the fabrication pattern of LbL self-assembly requires bridging layers between adjacent conducting layer or surface modification of conducting materials, harassing the conductivity of the whole film. Moreover, with the increase of deposition cycle, the conductivity of the film could be improved, while the transparency of the film will be reduced at the same time. Thus how to realize LbL film with high conductivity without sacrificing the transparency of the film remains a challenge. Even though metallic NW based LbL TCFs could deliver a moderate conductivity with a good transparency, the surface roughness of these NW TCFs are relatively high, which hinders their applications where a smooth surface is favorable, such as in organic thin film devices. Besides, metallic NW based LbL TCFs also suffer from poor electrochemical stability due to their redox activity in electrolytes.[108] Thus surface modification and encapsulation of metallic NW based LbL TCFs to obtain a smooth conducting film with improved electrochemical stability is desired.

2.5 PhD Studies in Contest with Literature

In this thesis, we focus on developing new strategy to fabricate LbL film for electrochemical applications, aiming to investigate possible solutions for the challenges as discussed above. Different from the traditional LbL deposition that uses individual polymers to fabricate multilayer films, we use polymeric complexes as the building blocks. Taking advantages of the features of polymeric complexes, multilayer films with fast growth behaviour as well as specific structures and functions for electrochemical applications are developed.

For electrochromic active layer, we developed negatively charged polyelectrolyte complexes to be complementary part for PANI. The specific features of polyelectrolyte complexes, such as large dimensions, charge accumulation and steric effect of the complexes led to a fast growth LbL film with porous structure. Moreover, by tuning the components, the complexes can also act as protons holder, promoting the electrochemical reaction of PANI. This is the first time that polyelectrolyte complexes are investigated and play important roles in LbL films for electrochemical studies.

For solid polymer electrolyte layer, we incorporated cyclodextrin supramolecular inclusion complexes into LbL self-assembly. Taking advantage of the unique configuration of inclusion complexes, the film showed lower glass transition temperature. Moreover, pathways for ions transportation inside the film was provided by cyclodextrin. It is known that to incorporate functional species as individual building blocks into LbL films is limited by several factors, such as whether there is compatible complementary part to assemble the film from the aspects of driving force and assembling conditions, and whether the functional species could realize their functionalities with the restriction of the complementary part and the confined distribution inside the LbL film. In this study, components with specific function were introduced into LbL assembly in the form of polymeric complex. The CDs were directly decorated on the PEG in the complexes and contributed as the pathway for the Li^+ ions. In this way, the functional species could not only take effect as expected, but also avoid to affect the construction of the multilayer film—it is still possible to find a suitable complementary candidate based on PEG, rather than based on CD only.

For transparent conducting layer, we adopted PEDOT:PSS conducting polymer complexes to form over-coated LbL layer onto Ag NW based conducting networks, in order to deliver TCF layer with

a relatively smooth surface. Considering the electrochemical activity of PEDOT:PSS, the over-coated layer could also act as passivation layer for Ag NW to protect Ag from oxidation and corrosion during electrochemical reactions. Even though the LbL self-assembly presents certain inherent drawbacks on TCF fabrication, it is demonstrated that this technique could make contributions to TCF layer by employing proper building blocks with desired functionalities.

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Chapter 3

Experimental Methodology

Materials and polymeric complexes designs are important to realize functional LbL films. This chapter first presents the rationale for material selection to achieve functional LbL films, and the underlying principles of their functionalities. Then, the designs of polymeric complexes with different expected contributions are discussed in detail. The techniques applied to characterize the growth behavior, morphology, optical and electrical properties of the LbL films are introduced. Finally, the film deposition process and the structures of the testing cells will be described in detail.

3.1 Rationale for Materials Selection

3.1.1 PANI as electrochromic active material

The mechanism of electrochromic conjugated polymers relies on the change of the π -electron states accompanied by reversible insertion/ extraction of ions during the redox reaction. These polymers show semiconducting behavior with an energy gap between HOMO and LUMO under their neutral states. The band structure will be modified when there is electrochemical doping (p-doping for oxidation and n-doping for reduction), leading to the lowered energy for intra band transitions and the formation of charged carriers (polarons and bipolarons).[1] The changes on band structure results in variation in optical properties, and the density of the charge carriers are responsible for the conductivity of the materials.

Polyaniline is one of the most widely studied EC polymers. The structure of non-conducting form of PANI could be illustrated as follows:

Figure 3.1 Chemical structure of PANI.

In principle, PANI could undergo continuous oxidation reaction, resulting in oxidation states from fully reduced leucoemeraldine state ($y=1$) to fully oxidized pernigraniline state ($y=0$). The most accepted model of the redox reaction of PANI is represented in Figure 3.2.[2] The change of molecular structure is responsive to the change of redox potential and pH. PANI possesses multiple colored forms depending on the oxidation state and the degree of protonation of the polymer film, including bright yellow for leucoemeraldine base state (LB, $\lambda_{\max} \approx 330\text{nm}$), and dark violet for pernigraniline base state (PB, $\lambda_{\max} \approx 550\text{nm}$). The intermediate oxidation state, emeraldine base ($y=0.5$, EB), could be protonated in a non-redox reaction, which results in greenish, electrochemical conducting emeraldine salt (ES, $\lambda_{\max} \approx 800\text{nm}$).[3] Compared with other EC polymers, PANI offers a simple platform for polyelectrochromism without the need of chemical derivatization of the monomers, such as derivatives and copolymers of polypyrrole.

In our study, PANI was adopted as electrochromic active material and complementary building blocks with polyelectrolyte complexes for LbL electrochromic layer fabrication.

Figure 3.2 Illustration of electrochemical oxidation states of PANI.[2] Reproduced from Ref. 2 with permission from Elsevier.

3.1.2 The most classical SPE matrix: PEO and PEG

Poly(ethylene oxide) or PEO, $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$, was the first polymer used as a solid solvent for lithium salts, LiX, to form polymer electrolytes.[4] PEO, with flexible ethoxy segments and the strong donor character of the ether oxygens (EOs), readily solvates Li^+ cations. Due to its high solubility of lithium ions, PEO is one of the most classical and most widely studied polymer host for the solid polymer electrolyte.

In PEO-LiX system, each lithium ion only associates with one polymer chain and there is no ionic cross-linking. Studies show that the coordination number of the lithium cation is 5, one of which is the anion of the lithium salt, and the remaining ligands are ether oxygen atoms on PEO chain. The transportation of lithium ions in PEO matrix relies on the local relaxation and segment motion of the PEO chains, which could be illustrated in Figure 3.3.[5]

Figure 3.3 Illustration of lithium ions movement in PEO matrix.

Polyethylene glycol (PEG), possessing the same repeat unit with PEO, is known as oligomers and polymers with molecular weight below 20000. The mobility of PEG chains are higher than that of PEO because of the shorter chains. However, at the same time, the shorter chains also facilitate the formation of crystalline phase, which is not beneficial for SPE. For both PEO and PEG, it is critical to suppress the formation of crystalline phase in the polymer matrix under room temperature. In our study, amine terminal PEG was chosen to limit the formation of the crystallized phase in PEG matrix (as shown in Figure 3.4). Polymer-supramolecular complexes were further prepared as building blocks for LbL SPE layer.

Figure 3.4 Molecular structure of the amine terminal PEG.

3.1.3 Conducting materials: Ag NW and PEDOT: PSS

Conducting films made from metallic nanowire (NW) network could provide high conductivity, at the same time, maintain a low metallic volume fraction, thus presenting high transparency.[6] Due to the flexibility of nanowire network, they could also be used for flexible devices, surmounting the rigid nature of inorganic based conducting electrodes, such as ITO and FTO. Ag NWs possess higher stability than Cu NWs and Al NWs, and are much cheaper than Au NWs. Solution processable Ag NWs have been extensively used for transparent conducting films, which are considered as promising substitutions of ITO based transparent electrodes.[7]

Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS) is the most widely studied and commercialized derivative of PEDOT because of its high conductivity and good optical transparency within visible region.[8] The most practical synthesis method of PEDOT: PSS is called BAYTRON P, which adopts $\text{Na}_2\text{S}_2\text{O}_8$ as oxidation agent and oxidatively polymerizes the EDOT monomer in the poly(styrenesulfonate acid) solution under room temperature.[9] The product is a dark blue PEDOT: PSS aqueous solution and could be easily processed for film fabrication. The chemical structure of PEDOT: PSS is shown in Figure 3.5. The PSS in the complex not only provide counter ions for passively doped PEDOT to balance the doping charges, but also help to stabilize PEDOT and form a coil structure with PEDOT in the aqueous solution, circumventing the poor solubility of polymerized EDOT.[10]

Figure 3.5 Illustration of chemical structure of PEDOT: PSS complex.[9] Reproduced from Ref. 9 with permission from John Wiley and Sons.

Thin films processed from PEDOT: PSS aqueous solution show anisotropic conductivity due to the layered structure of PEDOT: PSS thin films with PSS domain sandwiched between some PEDOT layers.[11] The in-plane conductivity of PEDOT: PSS film prepared by BAYTRON P method could be in a range of $1\text{--}10\text{ S cm}^{-1}$, while the out-of-plane conductivity is relatively poor.[9] The mechanism of lateral electrical conductivity of PEDOT: PSS film is based on the hopping of charge carriers along the conjugated polymer chains, which is revealed from its temperature dependence behavior.[8]

Because of the high conductivity, good transparency and good ductility under ambient conditions, PEDOT: PSS is considered as a suitable candidate for fabricating transparent and flexible conducting electrodes. In our study, we utilized PEDOT: PSS as building blocks to form capping layer with Ag network for LbL TCF preparation.

3.2 Polymeric Complex Synthesis

3.2.1 Polyelectrolyte-polyelectrolyte Complexes

Polyelectrolyte-polyelectrolyte complexes were formed by slowly adding the minor complexes component into the solution of major complexes component. For example, to prepare PAA-PEI complexes, PEI solution (4mL, 1 mg mL⁻¹, pH =7.45) were slowly added into PAA solution (30 mL, 2.3 mg mL⁻¹ pH =3.85) under stirring. Then the solution was stirred for 30 mins and filtered through 1µm filter to remove big particles. Other complexes were also formed in a similar way.

3.2.2 Polymer-polymer Complexes

Similar as synthesis method for PECs, PAA-PEO complexes were prepared by adding 6 mL (Mw~20,000, 2mg mL⁻¹, pH=2.85) PEO solution into 30 mL PAA solution (Mw~100,000, 2 mg mL⁻¹, pH=2.85) under mild stirring. The mixture would turn to a turbid suspension after a while, indicating the formation of PAA-PEO complexes. Excessive stir would cause dissolution of the complexes and the solution would become transparent. The PEO-PAA complex was synthesized by adding 3mL PAA solution into 30mL PEO solution under mild stirring.

3.2.3 Host-Guest Supramolecular Complexes

Cyclodextrins, composed of 5 or more α -D-glucopyranoside units linked 1 to 4, are of the most famous and well-studied host candidates in supramolecular chemistry. They have lipophilic inner cavities and hydrophilic outer shells. Most of them are natural products. The most notable feature of CDs is that they could form inclusion complexes with a wide range of guest compounds via

supramolecular interaction. In these complex compounds, the guest compound itself or the specific part are hosted inside the cavity of CD. The formation of these complexes is not only based on supramolecular interaction, but also relying on the dimensional coincidence between the cavity of CD and the guest candidate.[12] There is no covalent bond formed or destroyed during the formation of inclusive complexes, and the formation is controlled by the dynamic equilibrium.[13] It should be noted that the properties of the guest compounds could be modified significantly when they form complexes with CDs, which makes CDs the most important macrocyclic hosts. What is more, the inexpensive and nontoxic features further enable CDs to be widely used in chemistry, biochemical studies, medical applications and food industry.[14-17] Typical CDs contain 6-8 glucose monomers, referring to α -CD, β -CD and γ -CD, respectively (as shown in Figure 3.6).

Figure 3.6 Structures of cyclodextrins.[18] Reproduced from Ref. 18 with permission from The Royal Society of Chemistry.

PEG- α CD complexes were prepared by adding certain amount of α CD (depending on the ratio between ethylene glycol (EG) unit and α CD) into PEG-NH₂ solution (2 mg mL⁻¹, pH=2.85). The solution was stirred at 40 °C for 12 hours before being used for LbL assembly. PAA solution was prepared by diluting PAA concentrated solution using DI water. The final concentration was 2mg mL⁻¹ with pH=2.85.

3.2.4 Preparation of PEDOT: PSS Complexes Solutions

Different from PECs and other PCs discussed above, the PEDOT: PSS complexes is formed simultaneously with the oxidative polymerization of EDOT. In our study, we used diluted

commercialized PEDOT: PSS solution (0.8% in H₂O, conductive inkjet ink, Sigma-Aldrich) for the LbL capping layer fabrication on the Ag nw networks.

3.3 Characterization

3.3.1 FESEM

Surface morphology of the LbL films is characterized by field emission scanning electron microscopy (FESEM, JEOL 7600F). Figure 3.7 is the schematic of the main parts of a FESEM. The electron source is where a beam of electrons is generated. Then the electrons are accelerated and pass through the condenser lens, where the size of the electron beam is modulated. The focusing lens help to focus the electron beam onto the sample, and the scanning lens deflect the electron beam. The sample surface is scanned by the high energy electrons in a zig-zag pattern, generating a variety of signals at the surface of the studied solid surface.

The signals generated from electron-sample interactions could reveal many kinds of information of the sample surface, such as surface morphology, and elemental analysis. In our study, secondary electron images (SEI) are of the most interest. Secondary electrons are generated from the inelastic collision between the shell electrons of the sample surface and the electron beams. They are low in energy and sensitive to the surface roughness. SEI images are 2-dimensional images generated based on the signals of secondary electrons collected from a selected area of the sample surfaces, which are able to reveal the texture of the selected area.

The resolution of SEM relies on the nature of the electron beam, which could be described in Abbes equation:

$$d = \frac{0.61\lambda}{NA}$$

where d is the minimum resolvable distance, λ is the wavelength of the energy source and NA is the numerical aperture of the system. By increasing accelerating voltage, the λ could be reduced and the resolution could be improved (as high as several nanometers). However, higher

accelerating voltage could lead to deep penetration of the electrons into the sample, thus reducing the signals from sample surface.

SEM shows great advantages on providing morphological analysis as well as compositional information. The data processing is very fast and the resolution is relatively high. However, the application of SEM is limited to the solid surface. It is not suitable for liquid samples, or any unstable sample under high vacuum or high energy beam scanning. The sample size is also limited by the specimen chamber of SEM. Moreover, proper samples preparation should always be conducted in order to avoid artifacts.

Figure 3.7 A schematic of the main parts of a FESEM.

3.3.2 UV-Vis Spectrophotometer

Ultraviolet–visible (UV-Vis) spectrophotometer (Shimadzu, UV 2700) is used to study the film growth, optical properties as well as the chemical constitution of the LbL films. The basic principle relies on the characteristic absorption of certain functional group of ultraviolet or visible light. Molecules that contains bonding, non-bonding or π electrons could be excited to higher anti-bonding or non-bonding orbitals by absorbing ultraviolet or visible light. The wavelength of the light absorbed is directly related to the chemical constitution and configuration of the molecules. UV-Vis spectrophotometer could record the absorption of light by comparing the intensity of the

light generated from the light source before and after it passes through the sample. The transmittance (T) is described by the ratio of the intensity of the light past through the sample to the intensity of the light before passing through the sample. According to Beer–Lambert law, the absorbance (A) is described as:

$$A = -\lg T = \sum_{i=1}^N \kappa_i b_i c_i$$

where κ_i is the molar attenuation coefficient of species i in the sample, b_i is the path length of the light beam through the species i in the material sample and c is the concentration of the species i in the sample.

When UV-Vis spectrophotometer is used to monitor the growth of LbL film, the concentration of the materials on the substrates increases along with deposition cycles, thus the adsorption of light with certain wavelength will also increase. When the electrochromic active film is switched between different states by electrical field, the redox state of the materials will change, leading to different characteristic adsorption peaks. The difference on transparency or absorbance at certain wavelength between different states of the active film is used to describe the electrochromic behavior of the film. The UV-Vis spectrophotometer could provide fast analysis of the samples and the detection limitation are relatively low, which make it suitable for kinetic studies of the electrochromic behavior.[19]

The drawback of using UV-Vis spectrophotometer to study the electrochromic films or devices is that the contribution of the substrates and electrolyte cannot be completely excluded, even when the same kind of substrate and electrolyte are used as reference.

Figure 3.8 The configuration of a UV-Vis spectrometer.

3.3.3 Electrochemical Workstation

The electrochemical characterization of the LbL films are conducted on Solartron 1470E. The system could provide potentiostat and galvanostat channels that allow all traditional DC test and AC impedance test. The measurements are conducted in electrochemical cells, which contain three electrodes or two electrodes. A typical three electrodes system consists of a working electrode, a counter electrode and a reference electrode. The working electrode is a conductive electrode loaded with the material of interest. The chosen conductive electrode should be able to carry current flow and should be non-reactive with the loaded material or the electrolyte. A counter electrode is usually a noble metal which is stable under the test environment, such as Pt and Au. It is the auxiliary electrode of the working electrode, providing a close current loop. Reference electrodes are well-known electrodes that have accurately maintained electrode potential, such as Ag/AgCl electrode, saturated calomel electrode and standard hydrogen electrode. The reference electrode in a three electrode system is used to determine the potential of the working electrode. During the electrochemical reaction, high input impedance will be applied on the reference electrode to make sure there is no current going through the reference electrode and the potential of the reference electrode could maintain a constant potential. During the test, either the current flow or the potential of the working electrode will be monitored and controlled by the workstation, providing requested current or potential.

3.3.4 Electrochemical Impedance test

Electrochemical impedance is measured by applying an AC potential onto the electrochemical cells. The measurement is done with a very small excitation signal so that the behavior of the testing cells is pseudo-linear. In a pseudo-linear system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.

The excitation signal could be expressed as:

$$E_t = E_0 \exp(j\omega t)$$

where E_t is the potential at time t , E_0 is the amplitude of the signal, and ω is the radial frequency; and the current response as:

$$I_t = I_0 \exp(j\omega t - \phi)$$

where I_t is the response signal and has a different amplitude than I_0 , ϕ is the shifted in phase; then, the impedance is described as:

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0(\cos \phi + j \sin \phi)$$

The Nyquist plot is a parametric plot of a frequency response extracted from the AC impedance test. In a Nyquist plot, the real part of $Z(\omega)$ is plotted on the X-axis and the imaginary part is plotted on the Y-axis. The equivalent circuit of the testing cell could be deduced from the Nyquist plot, delivering import information of the device, such as equivalent series resistance, charge transfer resistance, time constant and diffusion behavior.[20]

3.3.5 Four Point Probe

Sheet resistance of the LbL conductive films were measured by four point probe. As illustrated in Figure 3.9, a four point probe contains four collinearly placed probes. During the measurement, a constant current I flows through the outer probes, and the voltage V between the two inner probes is monitored. The resistance of a square sample R_s could be described as:

$$R_s = A \frac{V}{I}$$

where A is the correction factor.[21]

Figure 3.9 The configuration of a four point probe.

3.4 Testing Cell Fabrication

3.4.1 3-electrode testing cell for EC film

The electrochemical characterization was done on 3-electrode testing cells. Each testing cell consisted of a Ag/AgCl as reference electrode, a Pt plate as counter electrode and the EC film on the ITO-coated glass as working electrode.

3.4.2 2-electrode testing cell for SPE layer

The ionic conductivity test was determined from AC impedance test of a 2-electrode testing cell. The testing cell consisted two ITO-coated glass slides placed in parallel and the LbL film sandwiched in between. The LbL film was first deposited on one of the electrode, and the other electrode was pressed onto the film directly. The as-assembled testing cell was clamped by clips to ensure good contact between the LbL film and the electrodes. The devices were kept in humidity chamber under 52% RH at room temperature (around 25 °C). When the effect of humidity on the ionic conductivity of SPE was studied, the relative humidity inside the chamber was controlled at certain level, and the testing cells were stabilized in the chamber for at least 24 hours before the test. When the contribution of temperature to the ionic conductivity of the LbL films was evaluated, the testing cells are stabilized onto a heater at certain temperature for about 10 mins before the impedance test.

3.5 Overview of Methodologies

In this chapter, we first presented the rationale for our material selections for LbL electrochromic layer, SPE layer, as well as transparent conducting layer. PANI was employed as electrochromic material due to its facile doping process as well as large optical modulation. PEO is the most classical polymer matrix for SPE. Its chemical synonymous, PEG, could provide high lithium ion solubility as well as moderate chain mobility. Thus PEG was chosen for SPE matrix. α CD possess special steric configuration and is able to form supramolecular complexes with a wide range of guest materials. In our study, α CD was adopted to form complexes with PEG via host-guest interaction as well as provide pathway for lithium ions transportation along the PEG backbone. Then, detain information of PC formation was provided. Preparation conditions for different kinds of PCs were discussed. After that, basic principles of characterization methods, such as FESEM, UV-Vis spectrometer, electrochemical work station, electrochemical impedance test, as well as four point probe, were illustrated. Finally, the structures of test cells for electrochromic characterization and ionic conductivity evaluation were presented.

In conclusion, this chapter presented our comprehensive understanding of the materials and characterization techniques involved in our study, ensuring a feasible approach towards our research targets.

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Chapter 4*

Layer-by-Layer Deposition of Polyelectrolyte Complexes for Electrochromic Active Layer

Electrochromic active layer is the core component of an electrochromic device. Traditional Layer-by-Layer (LbL) self-assembly using polymers as building blocks possesses inherent limitations when it is used in fabrication of electrochromic active layer. In this chapter, a facile method for rapid deposition of electrochromic active layer by using selected polyelectrolyte complexes (PECs) instead of individual polymers as building blocks is demonstrated. First, the designs of PECs for LbL assembly are discussed. Mono PEC system is proved to be superior to dual PECs system for electrochemical active layer fabrication. Moreover, the PECs candidates are further optimized using two weak polyelectrolytes. Finally, a fast growth electrochromic active layer with enhanced electrochromism via LbL self-assembly is demonstrated. The growth behaviour, morphology, electrochemical properties and electrochromic behaviours of the resultant films are systematically investigated.

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4.1 Introduction

Electrochromic materials comprise of redox-active species that exhibit significant, lasting and reversible changes upon coloration when electrons and cations such as H^+ or Li^+ are injected or withdrawn reversibly. The intercalation/de-intercalation of these small ions within the active material matrix widens/narrows the electronic band gap, resulting in differing wavelength absorptions, thus displaying the complimentary visible or non-visible wavelengths. For example, an electrochromic material can switch from a clear form to a colored form when it is oxidized, or vice versa.[1]

Unlike light emitting diodes which are associated with active emissive mechanism, the operation of devices utilizing electrochromic materials is based on passive transmissive mechanism in which the visual effects are accounted by modulation of light. Moreover, electrochromic materials need only an initial current pulse at a sufficient driving potential to initiate the electrochemical reaction, which requires low power consumption.[2, 3] Thus electrochromic materials are promising for non-emissive display and energy conservation applications, such as electronic paper, active thermal control and smart windows.[3, 4]

Among different types of electrochromic materials, conjugated conducting polymers have attracted great interests.[5, 6] Polyaniline (PANI), an important polymer that exhibits electrochromism, is capable of multiple redox transitions needless of chemical derivatization of the monomer. Therefore, PANI offers a simple platform for polyelectrochromism. The most commonly studied strategy for LbL electrochromic films is based on the electrostatic interaction between polycations and polyanions.[7] Pioneer work of PANI based LbL electrochromic film was done by Hammond and co-workers.[8] They successfully fabricated an electrochromic full device with the PANI/poly(2-acrylamido-methane-s-propanesulfonic acid) (PAMPS) multilayer film as one electrode and poly(3,4-ethylene-dioxythiophene)-poly(styrene sulfonated) (PEDOT:PSS)/linear poly(ethylene imine) (LPEI) as the complementary electrode. The device could change color reversibly with a semi-solid electrolyte as ionic conductor. Thereafter, PANI based electrochromic multilayer LbL films have been widely explored, including polymeric films

such as PANI/PSS,[9] PANI/poly(vinyl sulfonate) and PANI/poly(acrylic acid);[10, 11] polymer-inorganic hybrid films such as PANI/Prussian Blue and PANI/V₂O₅ multilayers;[12, 13] and films with incorporation of carbon materials, which could facilitate electrons transfer within the films, such as PANI/GO.[13] Recently, Lu and co-workers prepared starlike polyaniline-tethered silsesquioxane (POSS-PANI) nanocage, and successfully fabricated (POSS-PANI/PAMPS)_n and (POSS-PANI/sulfonated-PANI)_n films.[2] These films showed enhanced coloration modulation and elevated kinetics compared to PANI films prepared with other methods.[14, 15] The improvement resulted from the loosely packing structure introduced by the starlike molecular architecture of POSS-PANI and the unique morphology created by LbL assembly.

However, this kind of LbL approach usually suffers from slow process (<20 nm h⁻¹) and requires quite long time for the film preparation. Tens and even hundreds of layers need to be deposited in order to incorporate enough active materials for demanded optical modulation.[16-18] Moreover, the compact structure of the traditional LbL films is undesirable for the redox reaction of the electrochemical active materials.[19] Novel strategy to fabricate LbL films for electrochemical studies is highly demanded. Polyelectrolyte-polyelectrolyte complexes (PECs), consisting of two oppositely charged polyelectrolytes, possess large dimensions and charge accumulation. As discussed in Chapter 2, PECs are expected to be promising candidates for fast growth LbL films with porous structures. Even though the application of polyelectrolyte complexes (PECs) has attracted lots of interests, the advantage of using them in electrochemically functional films has not been exploited. Noting the potential to enhance electrochemical kinetics with the porous structures and the rapid film growth rates, it is of great interest to exploit the potential of polymeric complex for electrochromic layers and realize superior electrochemical performance.

In this work, we firstly discussed the suitable designs of PECs for electrochromic layers. The dual PECs system could achieve fast growth LbL with porous structure, while the electrochemical activity was very poor. Then we further optimized the components of PECs, and two weak linear polyelectrolyte poly(acrylic acid) (PAA) and polyethylenimine (PEI) were adopted to form PAA-PEI complexes. We demonstrated the rapid fabrication of LbL EC films by alternatively depositing negatively charged PEC PAA-PEI with PANI as electrochemical active material. We investigated the structure, morphology and rapid growth behavior of the LbL films. We further illustrated the

benefits of having the complex as building blocks in LbL films during electrochemical reaction. It was demonstrated that using PECs as building blocks for LbL deposition could help to obtain desirable electrochromic properties compared with films fabricated by individual polymers.

4.2 Experimental Methods

4.2.1 PECs Preparation

PANI solution was prepared according to the literature.[20] Firstly, 100 mg PANI powder was dissolved in 10 mL dimethylformamide and was subsequently put in ultrasonic bath for at least 2 h. The solution was further stirred for 12 hours and filtered with 0.22 μm filter. Then the PANI solution was added dropwise into pH adjusted DI water (pH =2.85) under vigorous stirring, with a final concentration 0.5 mg mL⁻¹.

Poly(styrene sulfonate) (PSS)-PANI complexes solution was made by slowly dropping 15 mL 0.5 mg/mL PANI solution into 12 mL 5.0 mg/mL PSS (pH=2.85) solution with a final ratio of PSS:PANI equal to 0.63 (molar ratio calculated by polymer unit, the same hereafter). PEI-PSS complexes with positive charges were made by adding 7 mL 2.5 mg/mL PSS solution (pH=2.85) into 30mL 1mg/mL PEI solution (pH=2.85), with a ratio of PEI:PSS equaling to 5.3. PSS-PEI complexes with negative charges were made by adding 4 mL 1 mg/mL PEI solution (pH=2.85) into 30 mL 2.5 mg/mL PSS solution (pH=2.85), with a final ratio of PSS:PEI equal to 4.71. PAA-PEI complexes suspension was made by slowly adding 4 mL PEI solution (pH =7.45; 1 mg mL⁻¹) into 30 mL 2.3 mg mL⁻¹ PAA solution (pH =3.85) under stirring, with a final ratio of PAA:PEI equalto 14.7. All the solution was stirred for 30 mins and filtered through 1 μm filter to remove big particles. After filtration, the complex suspensions can remain stable during the whole LbL assembly process.

4.2.2 Fabrication of electrostatic interaction based LbL film

Quartz slides were treated in piranha solution (1:3 mixture of 30% H₂O₂ and 98% H₂SO₄), heated at 80 °C for 20 mins. (*Caution: Piranha solution reacts violently with organic material and should be handled carefully.*) Indium Tin Oxides (ITO) coated glass slides (15 Ω sq⁻¹) were cleaned by 15 mins intervals of sonication in acetone, methanol and Milli-Q water. Before assembly, ITO-glass substrates were treated by oxygen plasma for 2 mins in order to get a negatively charged hydrophilic surface. To fabricate the PANI/PAA-PEI multilayer films, the freshly cleaned substrates were firstly immersed into PANI solution (pH=2.85) for 10 mins, followed by rinsing in pH -adjusted DI water bath (pH=2.85) twice (2 mins for each time). Then the substrates were immersed into PAA-PEI complex suspension (pH=3.85) for 5 mins and rinsed in pH-adjusted DI water (pH=3.85) twice (2 mins for each time). This procedure was repeated n times to fabricate an n double-layer film. After assembly, the films were air-dried and heated at 60 °C for half an hour. There was no interval drying step before the end of film fabrication. Other multilayer films were prepared in a similar way.

4.2.3 Characterization

Particle size and Zeta potential of the polyelectrolyte complexes were recorded on a Malvin Zetasizer Nano Series 90 at room temperature. The morphology and the thickness of multilayer films were characterized and determined by field-emission scanning electron microscopy (SEM, JEOL 7600F). The extracted thickness data was further confirmed by surface profiler. The sample roughness was measured using Atomic Force Microscope (AFM) with a DI 3100 (Veeco, Digital Instruments). Ultraviolet-Visible (UV-Vis) spectra were recorded on a UV-Vis spectrophotometer (Shimadzu UV3600). The *in situ* spectro-electrochemical properties of individual films were carried out in a quartz cell at room temperature in the UV-Vis spectrophotometer. The voltage supply was from Solartron 1470E. Cyclic voltammograms (CV) were performed on an electrochemical analyzer (Autolab Potentiostat, PGSTAT302N). The three-electrode cell consisted of Ag/AgCl as the reference electrode, Pt as the counter electrode and the as-synthesized LbL film on ITO-glass as the working electrode. The electrolyte used was 1 M LiClO₄ in PC. The

electrochemical impedance spectrum (EIS) tests were conducted in the frequency range of 1 MHz to 0.1 Hz with the signal amplitude of 10 mV under open circuit voltage using Solartron 1470E.

4.3 Results and Discussion

4.3.1 Dual polymeric complexes LbL film: [PSS-PANI/PEI-PSS]_n

First, we designed a dual polymeric complexes (PCs) system with positively charged PSS-PANI complex and negatively charged PEI-PSS complex as building blocks. It is supposed that a dual PC system could harness the advantages of PC to the utmost extent, maximizing the possibility of achieving porous films.

It is well-known that the intermediate oxidation state (emeraldine base, EB) of PANI can be protonated by small-molecule acids and lead to the formation of the green color, electrically conducting emeraldine salt (ES) form. When the concentrated PANI in DMF solution was dropped into the pH adjusted DI water, the color of the PANI solution changed from dark blue to green, which indicated the formation of PANI ES solution. During the whole LbL film fabrication process, the pH of the PANI aqueous solution was strictly kept at 2.85. Under this condition, PANI was protonated, leading to the formation of positively charged ES solution. [13, 21]

The driving force for the PSS-PANI complex formation was mainly based on electrostatic interaction between protonated amine groups on PANI and the sulfonic groups on PSS. After optimizing the PC preparation conditions, stable PSS-PANI complexes and PEI-PSS complexes solutions were obtained as described before, with average diameters of 185 nm and 188 nm, respectively. The PSS-PANI complexes in aqueous showed a ζ potential of -36.6 mV, which indicates that the surface of the complexes was dominated by sulfonic groups. The PEI-PSS complexes suspension showed a ζ potential of +46.8 mV, indicating the surface of the complexes was covered by large amount of protonated amine groups carried by PEI.

The surface morphology of films with different deposition cycles was characterized by FESEM, as showed in Figure 4.1. In the first several deposition cycles, only small amount of PSS-PANI and PEI-PSS complexes were deposited on the substrates as indicated by the thickness. It was discussed that the complexes began to cover the substrate at this stage.[22] The film then grew rapidly with the further increased deposition cycles, associated with a rougher surface. As shown in Figure 4.1c-d, 15 bilayers PSS-PANI/PEI-PSS film already showed distinct porous structures, while $[\text{PANI/PSS}]_{15}$ film, which was fabricated under the similar condition using uncomplexed PANI and PSS, was quite thin and showed compact structure. From the cross-section image of the $[\text{PSS-PANI/PEI-PSS}]_{15}$ film, two kinds of pores could be distinguished: the pores embedded in the film and the through-pores throughout the film. The porous structure was formed by loosely packed sphere-like particles, which originated from agglomeration of oppositely charged polyelectrolytes complexes. It should be noticed that the thickness of $[\text{PSS-PANI/PEI-PSS}]_{15}$ film was around 260 nm, which was much smaller than 15 times of the sum of the average diameters of the two polyelectrolytes complexes used. This phenomenon could be resulted from the deformation and shrinkage of the complexes when deposited on a solid surface.[23] Considering the large dimension and repulsion between same charged complexes, it required several deposition cycles just to cover the whole substrate surface without much growth on film thickness. Similar phenomena also happened to other LbL films fabricated by polyelectrolyte complexes studied later, and could also be explained by the same reasons.

Figure 4.1 (a-c) FESEM images of $[\text{PSS-PANI/PEI-PSS}]_n$ films for (a) $n=5$, (b) $n=10$, (c) $n=15$; (d) FESEM image of $[\text{PANI/PSS}]_{15}$; (e) cross-section image of $[\text{PSS-PANI/PEI-PSS}]_{15}$.

$[\text{PSS-PANI/PEI-PSS}]_{15}$ films were chosen for electrochemical test. Cyclic voltammetry test was done under a potential window of -0.2 V to 0.9 V in $0.5\text{ M H}_2\text{SO}_4$ electrolyte, which was normally used for PANI based electrochromic films. As shown in Figure 4.2a, two pair of redox peaks could be observed, which were referred to two accessible oxidation/reduction reactions for PANI with color changes. The first pair of redox peaks would be corresponding to reversible yellow-green transformation and the second pair of redox peaks would be corresponding to reversible green-blue transformation. Considering the obvious color difference between oxidized state PANI (blue) and reduced state PANI (pale yellow), the contrast should be able to be observed by naked eyes. However, the film did not show any optical color change during redox process and the redox current was quite low, indicating that only very small amount of active materials participated in the electrochemical reaction. When different scan rates were applied, the peak potential separation ΔE_p was constant, which indicated relatively low resistance. And the peak heights grew linearly

with the increasing scan rates, which suggested fast ion transfer during redox process. Based on all these information observed from cyclic voltammograms, it was assumed that only a small amount of PANI in the film in vicinity to electrode contributed to the reaction, that is to say, only the PANI involved in first several layers deposited on the electrode was electrochemical active during the redox reaction. Further test on the films with different deposition cycles showed that with the same testing area, the redox current of 15 bilayers film was not much higher than that of 3 bilayers film (as shown in Figure 4.2b), which proved that only the first several layers took part in the electrochemical reaction while the following layers barely contributed to the electrochemical performance of the whole film. It may result from the specific porous structure of these films: big channels and holes arisen from loosely packed of polyelectrolyte complexes indicated poor connection of active materials. Considering PANI was the only electrochemical active materials under test condition and associated with PSS as negatively charged complexes, it was quite possible that from certain layer, the film became insulating for PANI to have electrochemical reaction. Further improvement on the building blocks design for LbL films and deposition conditions are needed in the future work to achieve satisfactory electrochemical properties.

Figure 4.2 (a) Cyclic voltammetry curves of $[\text{PSS-PANI/PEI-PSS}]_{15}$ under different scan rates; (b) Cyclic voltammetry curves of $[\text{PSS-PANI/PEI-PSS}]_n$ films with different deposition cycles at 20 mV/s, blue: $n=0$ (bare ITO-coated glass substrates), red: $n=1$, black: $n=3$ and pink: $n=5$.

4.3.2 Mono PEC LbL film: $[\text{PANI/PSS-PEI}]_n$

The reason for $[\text{PSS-PANI/PEI-PSS}]_n$ films exhibited electrochemical activity at the first several bilayers only was firstly attributed to the polyanion part, PEI-PSS, of the $[\text{PSS-PANI/PEI-PSS}]_n$ films. It was assumed that the polyelectrolyte complex PEI-PSS layers cut off the path for electrons transfer due to the inherent insulation and the large dimensions of the complex. To inspect this assumption, $[\text{PSS-PANI/PEI}]_n$ films were fabricated in the similar way. However, similar to the $[\text{PSS-PANI/PEI-PSS}]_n$ films, only the first several bilayers showed electrochemical activity and the following layers had little contribution. Considering the findings in 4.3.1 that PANI tends to form the core of the complex even though the concentration ratio of PSS: PANI was only 0.63, and the zeta potential of the PSS-PANI complexes was quite low, it was indicated that PSS was the dominant component of the complex. The reason for the poor electrochemistry properties of both $[\text{PSS-PANI/PEI-PSS}]_n$ and $[\text{PSS-PANI/PEI}]_n$ were attributed to the rigid structure and inherent insulation of PSS. In the previous work, PSS in PSS-PANI complexes was added into PANI solution after PANI was doped by HCl. Under this condition, the shielding effect of PSS in the outside part of the complex may cause large chemical inertness and retard the electrochemical reaction. Based on these considerations, LbL films with mono PEC system $[\text{PANI/PSS-PEI}]_n$ were fabricated and studied.

Unlike $[\text{PSS-PANI/PEI-PSS}]_n$, $[\text{PANI/PSS-PEI}]_n$ did not show obvious porous structure (Figure 4.3a-b). With the same deposition cycles, $[\text{PANI/PSS-PEI}]_n$ films were much thinner than $[\text{PSS-PANI/PEI-PSS}]_n$, even though PEI-PSS complex used in 4.1 and PSS-PEI complex had similar dimensions (around 180nm). UV-Vis absorption spectra were used to track the growth of this multilayer film. From Figure 4.3(c), it could be clearly observed that the absorption increased along with the deposition cycles. Absorbance at 578 nm was extracted for analysis. Simple exponential models and linear models were applied to fit the trend of the absorbance. As shown in Figure 4.3(d), the trend of first 8 bilayers' absorbance fitted well with exponential growth with $R^2=0.998$ at 578 nm. The growth of following bilayers after 8th bilayer showed weak tendency of linear growth, which was consistent with the exponential growth behaviour discussed in Chapter 2.

Figure 4.3 (a-b) FESEM images of $[\text{PANI/PSS-PEI}]_{30}$ films; (c) UV-absorption spectra of $[\text{PANI/PSS-PEI}]_n$ multilayers assembled on quartz slides ; (d) absorption as a function of deposition cycles at 578nm.

Electrochemical test was applied on $[\text{PANI/PSS-PEI}]_{30}$ films. Figure 4.4 showed the cyclic voltammograms of $[\text{PANI/PSS-PEI}]_{30}$. Compared with $[\text{PSS-PANI/PEI-PSS}]_{30}$ films, the redox current of $[\text{PANI/PSS-PEI}]_{30}$ films was much higher, indicating that most of the PANI in the films was electrochemically active during the reaction. It demonstrated that for LbL self-assembly, the mono PEC system was more suitable than dual PCs system in application of electrochromic layer fabrication.

Figure 4.4 Cyclic voltammetry curves of $[\text{PANI/PSS-PEI}]_{30}$ under different scan rates.

4.3.3 LbL film with designed structure and enhanced electrochromism: $[\text{PANI/PAA-PEI}]_n$

In previous work, PSS was used to form polyelectrolyte complexes considering that PSS was stable in the solutions under broad range of pH. The pH of PEI solutions was also controlled below 3, so that the protonation degree of PEI was very high and the polymer chains were highly extended. Under these conditions, it was relatively easy to get stable polyelectrolyte complexes. However, the films were more compact than the dual PC system. When compared to $[\text{PANI/PSS}]_{30}$ system, the advantage of using PC on electrochemical performance was barely observed. Thus how to strengthen the contribution of PC on LbL film construction as well as on the electrochemical properties of the resultant films need to be further considered.

PAA, unlike PSS, is a weak polyelectrolyte, of which the configuration highly depends on the pH of the solution. Under high pH, the carboxyl groups are dissociated and the polymer chains tend to be extended. On the contrary, the carboxyl groups of PAA are highly protonated under low pH environment, and the polymer chains tend to curl up and become more hydrophobic, which is favorable for forming porous structure during LbL process.[24, 25] Moreover, highly protonated PAA will carry large amount of H^+ into the film, which would be conducive to the oxidation process of PANI. Even in $[\text{PANI/PSS-PEI}]_n$ films, PEI was also highly protonated. The species directly interacting with PANI was PSS, which is a strong polyelectrolyte and could barely carry

protons. Thus PAA under low pH is a promising candidate to work with PEI as a dual proton carriers system for improving electrochemical properties of PANI based LbL film.

Characterization of polyelectrolyte complexes

As mentioned above, highly protonated PAA is beneficial for forming porous structure. However, the formation of PAA-PEI complexes is driven by the electrostatic interaction between the protonated amino groups on PEI and the dissociated carboxylic acid groups on PAA. Thus in order to form a stable LbL system with specific porous structure, the protonation degree of PAA has to be carefully controlled to form stable PAA-PEI complex, at the same time maintaining certain hydrophobicity. Once the PEI solution was added into PAA solution, the solution became turbid and large floccules could be observed. The formation of large floccules was resulted from the uneven distribution of PEI in the solution, as well as the strong electrostatic interaction between PEI and PAA. The floccules disappeared after all the PEI solution was added under vigorously stirring, indicating a new equilibrium was established. The mixture was further stirred for 30 mins in order to get a stable PAA-PEI complex suspension. The size and ζ potential of the complex were recorded on Nanosizer. As shown in Figure 4.5, the PAA-PEI complexes exhibited an average hydrodynamic diameter of 342.5 nm, with ζ potential of -45.9 mV. The negative ζ potential indicated that PAA was the dominating component on the surface of the PAA-PEI complexes.

Figure 4.5 Size distribution of the PAA-PEI complex.

Layer-by-Layer assembly of rapid growing [PANI/PAA-PEI]_n multilayer films

[PANI/PAA-PEI]_n multilayer films were deposited by alternatively dipping the substrate in positively charged PANI solution and negatively charged PAA-PEI complexes suspension. Figure 4.6 illustrated the structure of PAA-PEI complexes and the deposition procedure for [PANI/PAA-PEI]_n multilayers. The driving force for LbL assembly was provided by the electrostatic interaction between cationic amino groups on the backbone of protonated PANI and those dissociated carboxylic acid groups on PAA and the surface of PAA-PEI complexes.[11, 26] In order to investigate the effect of polyelectrolyte complexes, PANI/PAA multilayer films, in which the negative charges species were free PAA polymers, were fabricated as control samples under the same conditions with PANI/PAA-PEI films.

Figure 4.6 Illustration of the structure of PAA-PEI complex and the deposition process of the multilayer films.[27] Reproduced from Ref. 27 with permission from John Wiley and Sons.

The surface morphology and cross-sectional view of the [PANI/PAA]₂₀ film and the [PANI/PAA-PEI]₂₀ film were shown in Figure 4.7. The film consisted of polyelectrolyte complexes displays obvious porous structures (Figure 4.7d and 4.7e), while the [PANI/PAA]₂₀ film possesses compact structure (Figure 4.7a and 4.7b). This porous structure originated from the relatively rigid structure of the electrostatically cross-linked PAA-PEI complexes as well as the strong electrostatic repulsion between the complexes, while the un-complexed PAA is more flexible and tends to self-

adjust its configuration to form a smooth surface during the deposition process.[23] The FESEM cross-section images (Figure 4.7c and 4.7f) showed that the thickness of $[\text{PANI/PAA-PEI}]_{20}$ film was around 430 nm, which is obviously larger than the thickness of $[\text{PANI/PAA}]_{20}$ (which is around 200 nm) under the same deposition condition.

Figure 4.7 (a,b) Top-view FESEM images of the $[\text{PANI/PAA}]_{20}$ film; (d,e) top-view FESEM images of the $[\text{PANI/PAA-PEI}]_{20}$ film; cross-section image of (c) the $[\text{PANI/PAA}]_{20}$ film, and (f) the $[\text{PANI/PAA-PEI}]_{20}$ film.[27] Reproduced from Ref. 27 with permission from John Wiley and Sons.

UV-Vis absorption spectra of $[\text{PANI/PAA-PEI}]_n$ and $[\text{PANI-PAA}]_n$ films with different deposition cycles further illustrated the process of film growth in the first 20 deposition cycles. As shown in Figure 4.8, the absorption peaks at about 320 nm were derived from the excitation of the benzene segment on polyemeraldine chains. The peaks near 430 nm were assigned to the polaron absorption, and the peaks at around 600 nm were originated from the quinoid segment on partially protonated polyaniline chains.[2, 26] The absorbance of the film increased as the deposition number increases, but the absorbance of the film with PAA-PEI complexes grew much faster than the film with free PAA. Thickness of the films as a function of number of bilayers was shown in Figure 4.9a. The thickness of $[\text{PANI/PAA-PEI}]_n$ films grew exponentially with the number of deposition cycles, while the thickness of $[\text{PANI/PAA}]_n$ increased linearly. The dash lines indicated the exponential fit (in red) and linear fit (in black), respectively. The rapid growth of polyelectrolyte complexes film thickness could be attributed to the larger dimensions of PAA-PEI complexes than pure PAA.[24] Avoiding intermediate drying step and tailoring specific pH of the dipping solutions also promoted the loose packing of PAA-PEI complex and PANI.[28] However, these could not help to explain why the absorption of the complex film was also higher than the film with free PAA, which meant there was more PANI in the complex film within the same deposition cycle.

Figure 4.8 UV-Vis absorption spectra of (a) $[\text{PANI/PAA}]_n$ multilayers and (b) $[\text{PANI/PAA-PEI}]_n$ multilayers assembled on quartz slides.[27] Reproduced from Ref. 27 with permission from John Wiley and Sons.

Figure 4.9 Dependence of the (a) thickness and (b) roughness of the $[\text{PANI/PAA}]_n$ and $[\text{PANI/PAA-PEI}]_n$ films as a function of the deposition cycles.[27] Reproduced from Ref. 27 with permission from John Wiley and Sons.

When further exploring the film growth mechanism, it should be noticed that the well accepted “in-and-out” diffusion mechanism for exponential growth behavior,[29, 30] which is based on the diffusion behavior of weak polyelectrolytes under restricted pH values, could not be fully applicable on this $[\text{PANI/PAA-PEI}]_n$ system. Even though both PAA and PEI are weak polyelectrolytes, the pH of all the dipping solutions in this work were kept at low values. Under this condition, the linear PEI was highly protonated and could interact strongly with PAA. Thus the mobility of PEI and PAA was restricted by the strong electrostatic interaction, which was not favorable for “in-and-out” diffusion.[31] Recently, a surface roughness induced exponential growth mechanism was proposed by Sun and his co-workers based on their study on LbL film composed of PVPON-PAA complexes.[23] They pointed out that with the increasing deposition cycles, the increased surface roughness led to increased surface area, which permitted more

building blocks to be deposited on the film than in the previous deposition cycle. In our present work, the relatively large amount of charges carried by the PAA-PEI complexes caused strong repulsion between the complexes, which resulted in the uneven distribution of the complexes when they adsorbed onto the film surface. Thus the films presented a porous structure with rough surface. The surface roughness of the films was monitored by AFM (as shown in Figure 4.10). The root mean square roughness of the LbL films was extracted and shown in Figure 4.9b. It could be seen that with the increasing deposition cycles, the roughness of $[\text{PANI/PAA-PEI}]_n$ films grew dramatically, while the surfaces of $[\text{PANI/PAA}]_n$ films were much smoother. For example, the root mean square roughness of the $[\text{PANI/PAA-PEI}]_{40}$ film was around 170 nm, while it was only around 50 nm for the $[\text{PANI/PAA}]_{40}$ film as measured using AFM. The surface roughness induced fast growth mechanism could give a clue to the phenomenon that the absorption of the complex film was higher than the film with free PAA. Therefore it is concluded that both the large dimensions of the polyelectrolyte complexes and the surface roughness induced exponential growth behavior contributed to the fast growth of $[\text{PANI/PAA-PEI}]_n$ films.

Figure 4.10 AFM images for [PANI/PAA-PEI]_n films: (a) n=5, (b) n=10, (c) n=20, (d) n=30, and (e) n=40.

Electrochromic properties of [PANI/PAA-PEI]_n films

Cyclic voltammetry of [PANI/PAA]₃₀ and [PANI/PAA-PEI]₃₀ films collected in 1 M LiClO₄ in PC were shown in Figure 4.11a and 4.11b, respectively. Two pairs of oxidation and reduction peaks of polyaniline could be recognized from the CV curves of both films under low scan rates. The oxidation peaks at lower potential came from the leucoemeraldine to emeraldine state transition, and the oxidation peaks at higher potential can be assigned to the transition from emeraldine to pernigraniline state.[32] It could be observed that the transition between the emeraldine and pernigraniline state of polyaniline was shifted to lower potential for [PANI/PAA-PEI]₃₀ films compared with [PANI/PAA]₃₀ films, which could be attributed to the existence of partially protonated PAA and PEI in the film. The substantial protons carried by PAA and PEI could affect the doping level of PANI and therefore regulate the electrochemical behavior of the LbL films. The contributions of protonated PAA and PEI were further illustrated and discussed with the EIS results and electrochromic characterizations. Under high scan rates, the potential separation between the oxidation and the reduction peaks of [PANI/PAA-PEI]₃₀ was smaller than that of [PANI/PAA]₃₀, indicating a more favorable electrochemical reaction in [PANI/PAA-PEI]₃₀ films with better reaction reversibility.[2, 32] The two pairs of redox peaks merged into one pair of wide redox peaks under high scan rates for [PANI/PAA-PEI]₃₀, because they were near to each other and the width of the peaks were broad. Similar phenomenon was also observed in other reported LbL films.[33, 34] The effective ion diffusion coefficient can be estimated by applying Randles Sevcik equation:[32, 35]

$$I_{peak} = 2.71 \times 10^5 \times A \times C \times D^{1/2} n^{3/2} \nu^{1/2} \quad (4.1)$$

where I_{peak} stands for the peak current, A is the electrode area, C is the concentration of species in the bulk, D represents for the diffusion coefficient, n refers to the number of electrons involved in the redox reaction and ν is the scan rate. As shown in Equation 4.1, the I_{peak} is proportional to $\nu^{1/2}$, and the D can be extracted from the slope as shown in Figure 4.12. The improved ion diffusion coefficient in [PANI/PAA-PEI]₃₀ films compared to [PANI/PAA]₃₀ films illustrated fast ion diffusion process in the porous films.

Figure 4.11 CV curves of the (a) [PANI/PAA]₃₀ film and (b) [PANI/PAA-PEI]₃₀ film under different scan rates in 1M LiClO₄ in PC.[27] Reproduced from Ref. 27 with permission from John Wiley and Sons.

Figure 4.12 Peak current I_{peak} as a function of square root of scan rate $v^{1/2}$, K stands for the slope of the line. According to Randles Sevcik equation $K = 2.71 \times 10^5 \times A \times C \times D^{1/2} n^{3/2}$.

Figure 4.13a and 4.13b presented the UV-Vis transmittance response of the [PANI/PAA]₃₀ and [PANI/PAA-PEI]₃₀ films under oxidized state and reduced state. The transmittance of [PANI/PAA-PEI]₃₀ was slightly lower than [PANI/PAA]₃₀ at all applied potentials, which is consistent with the difference in the film thickness. It was observed that the transmittance of both films decreased as the applied potential increases from -0.3 V to 0.9 V, where PANI was oxidized from LB state to PS state. The contrast (ΔT , $\Delta T = T_b - T_c$, where T_b and T_c are denoted as transmittance at bleached and colored states, respectively) was extracted at 630 nm. As shown in Figure 4.13c, the contrast of the [PANI/PAA-PEI]₃₀ film could reach up to $\Delta T = 28.7\%$, while the contrast of the [PANI/PAA]₃₀ film was only $\Delta T = 11.1\%$. The transmittance modulation of [PANI/PAA-PEI]₃₀ was higher than other PANI/polymer based LbL films reported in the literature,

such as [PANI/PNACN]₃₀ and [POSS-PANI/PAMPS]₅₀. [34, 36] The electrochromic performance delivered from the PANI/PAA-PEI LbL films is also comparable with that of PANI based EC films prepared by other technique and tested under similar conditions. For instance, PANI films prepared by electro-polymerization showed an optical contrast around $\Delta T=16.2\%$, which is lower than the contrast of the EC films prepared by the LbL strategy demonstrated in this study. [37] It is also reported that PANI derived from chemical oxidation of aniline and further processed into films by spin-coating or in-situ formed on ITO-glass substrates possessed coloration modulation of around $\Delta T=22\%$ and 28% , respectively, under similar testing conditions with those of our studies. [38-39] It has been suggested that the contrast of an electrochromic film is related to the amount of active material that can be intercalated with electrolyte ions. [4, 40] The fast growth behavior of [PANI/PAA-PEI]_n allowed a large amount of active material deposited into the film in a short time, while [PANI/PAA]_n only incorporated limited the amount of active material under the same condition. On the other hand, the introduction of the PAA-PEI complexes into the film led to porous structure, which provided large inner space of the films and ensures the interaction between PANI and electrolyte ions. These two characteristics of [PANI/PAA-PEI]_n have contributed to the higher contrast.

Figure 4.13 Electrochromic behaviours of the [PANI/PAA]₃₀ and [PANI/PAA-PEI]₃₀ films: (a) UV-Vis spectra of [PANI/PAA]₃₀ under varying potentials; (b) UV-Vis spectra of [PANI/PAA-PEI]₃₀ under varying

potentials; (c) transmittance versus time for switching time calculation at 630nm(in 1M LiClO₄ in PC).[27] Reproduced from Ref. 27 with permission from John Wiley and Sons.

Kinetics study was also conducted at 630 nm. The applied potential was switched between -0.3V and 0.9V. Switching time is described as 90% of the time taken for the completion of color conversion under kinetic test condition. For [PANI/PAA]₃₀ film, the coloration time is 6 s and the bleaching time is 24 s. Under the same condition, the films fabricated with PANI and PAA-PEI complexes display faster switching behavior with coloration time and bleaching time of 3 s and 15 s, respectively. The switching time could be affected by several factors such as film thickness, applied potential, ionic conductivity of electrolyte, and charge transfer resistivity.[41] Thick films usually possess longer switching behavior as the diffusion process is much slower than that in the thin films.[42] However, even though the [PANI/PAA-PEI]₃₀ was much thicker than the [PANI/PAA]₃₀ films in this work, the porous structure played an important role in enhancing the switching kinetics.[4, 41] It has been suggested that the electrochromic process involved double injection/extraction of electrons and ions from the film. In general, a compact film structure would lead to slow diffusion process and then long switching time.[2] The highly porous structure of [PANI/PAA-PEI]_n provided large reaction surface and inner space for electrolyte to penetrate into the film, shortening the ion diffusion pathways.[32, 38, 43, 44] This result was in accordance with a larger ion diffusion coefficient of [PANI/PAA-PEI]₃₀ as discussed earlier. Polymer-based EC films with porous structure are usually fabricated using template or specific deposition conditions.[45-47] In this work, we showed that porous EC films could also be fabricated by solution-processable method without any template or seed layers. Meanwhile, the dual weak polyelectrolytes in PAA-PEI complexes, which were highly protonated under the film deposition conditions, introduced large amount of protons into the film. These protons increased the conductivity of the intermediate oxidized PANI,[43] thus also facilitated the redox reaction. EIS measurements were conducted in a frequency range of 0.1 Hz to 1 MHz. The Nyquist plots of both [PANI/PAA]₃₀ and [PANI/PAA-PEI]₃₀ films are shown in Figure 4.14. The high-frequency semicircle corresponds to the charge- transfer impedance on the electrode/electrolyte surface. The inclined line in low frequency is related to the ion diffusion process. The smaller semicircle of [PANI/PAA-PEI]₃₀ indicated a lower charge- transfer resistance, and a more gradual slope signifies a faster ion-diffusion process.[47, 48] Coloration efficiency (CE) is defined by the following equation:[32]

$$CE(\lambda) = \frac{\Delta OD(\lambda)}{Q}; \Delta OD(\lambda) = \log \frac{T_b}{T_c} \quad (4.2)$$

where Q refers to the charge inserted into the film per unit area within the coloration time, and λ is the wavelength. It represents the change in optical density (OD) per unit of charge inserted in or extracted from the film. The extracted coloration efficiency is $24.8 \text{ cm}^2 \text{ C}^{-1}$ for $[\text{PANI/PAA-PEI}]_{30}$ and $12.9 \text{ cm}^2 \text{ C}^{-1}$ for $[\text{PANI/PAA}]_{30}$ at 630 nm. A higher value of CE indicates that the $[\text{PANI/PAA-PEI}]_{30}$ film provides larger optical modulation with a smaller intercalation charge density than $[\text{PANI/PAA}]_{30}$.

Figure 4.14 Nyquist plots of $[\text{PANI/PAA-PEI}]_{30}$ films and $[\text{PANI/PAA}]_{30}$ films. Insert shows the enlarged area of the high frequency region of the Nyquist plot.[27] Reproduced from Ref. 27 with permission from John Wiley and Sons.

4.4 Conclusions

In this chapter, we explored the possibility to use PECs as building blocks to build up fast growth LbL films as electrochromic active layers. Dual PECs system PSS-PANI/PEI-PSS was found to be helpful to fabricate porous films with fast growth behavior due to the large dimensions of the PECs as well as the charge accumulation and strong repulsion between PECs, while the electrochemical inertness of PSS in the PSS-PANI harassed the redox reaction of PANI. Thus mono PEC system PANI/PSS-PEI was developed to avoid this issue. This mono PEC system was further modified to PANI/PAA-PEI, which consisted of dual weak polyelectrolyte complexes PAA-PEI. Similarly, $[\text{PANI/PAA-PEI}]_n$ multilayer films exhibited rapid growth behaviour with obvious porous structure compared with traditional LbL film $[\text{PANI/PAA}]_n$, which was formed by PANI and uncomplexed polyelectrolyte. The fast growth behaviour enabled relatively large

amount of active materials, which was PANI in our study, to be deposited into the LbL film within a short time. Moreover, the porous structure of the films provided large active surface area for redox reaction and shortened the ion diffusion pathway. The involvement of PAA-PEI not only contributed to the growth behaviour and morphology of the resultant LbL films, but also promoted the electrochemical reaction of PANI. Compared to $[\text{PANI/PAA}]_n$ films, $[\text{PANI/PAA-PEI}]_n$ films presented enhanced optical modulation and improved kinetics.

This is the first time that PECs are introduced into LbL assembly as building blocks for electrochemical studies. Our work demonstrated that with careful design of the candidates of PECs and deposition conditions, it would be a facile method to use PECS as building blocks to fabricate fast growing LbL films with enhanced electrochemical properties, overcoming the drawbacks of traditional LbL assembly using individual polymers as building blocks. However, there are still some imperfections of this system. Detailed information will be discussed in Chapter 7, and further modification will be suggested.

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Chapter 5*

Hydrogen-Bonding-Directed Layer-by-Layer Deposition of Polymeric Complexes for Solid Polymer Electrolyte

The electrolyte layer in an electrochemical device is the ionic conductive layer that facilitates the redox reaction of the anode material and the cathode material. The solid polymer electrolyte possesses high mechanical stability, high chemical stability and high process safety, thus it is superior to the liquid electrolyte in terms of device fabrication. However, when applying Layer-by-Layer (LbL) technique on fabricating solid polymer electrolyte layer, the intrinsic features of electrostatic LbL films result in low ionic conductivity. How to improve the ionic conductivity of LbL in order to serve as solid polymer electrolyte layer remains a challenge. In this chapter, we demonstrate a new strategy to fabricate hydrogen-bond-directed LbL films with high ionic conductivity by using polymeric complexes as building blocks. First, the designs for suitable polymeric complexes for SPE layers are discussed. Then the design and characterization of a supramolecular complex is presented, which consists of special steric configuration that could be beneficial to ions transportation. The structural, morphological, thermal and electrical properties of the resultant LbL films are systematically investigated. Finally, the possibility to use the film as solid polymer electrolyte layer in an electrochromic device is explored.

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5.1 Introduction

In an electrochemical device, the electrolyte layer stays between the cathode material and anode material, communicating the redox reactions at the two electrodes by hosting and transporting ions. Compared with liquid and gel electrolytes, solid polymer electrolyte (SPE) films present robust mechanical properties and high thermal, chemical and electrochemical stability. SPE could provide wider range of operation temperature, easier processing as well as less corrosion issue of the electrode.[1-3] These characteristics endow SPE films as promising candidates for all-solid-state electrochemical device applications, such as dye-sensitive solar cells, batteries, displays, fuel cells, smart windows, and flexible devices.[4]

Poly(ethylene oxide) (PEO)/Li⁺ system is one of the most traditional and widely adopted system for SPE. This system is famous for the high solubility of Lithium salt in PEO matrix.[5] It was first discovered in 1973, and an all-solid-state battery with PEO/Li⁺ as SPE was successfully developed soon after that.[6] It has been revealed that it is the local relaxation and Brownian motion (segment motion) of the polymer chains that mostly dominated the ion transport in the SPE, both of which are believed to be more favorable in the amorphous phase of the host polymer.[2] However, it is quite easy for PEO to form the crystalline phase at room temperature (RT) and the ionic conductivity of the resultant film is quite low, which prevents its application where high ionic conductivity at RT is desired. Many efforts have been devoted to improve the performance of PEO/Li⁺ SPEs. Inorganic fillers[7] and organic plasticizers[8] were widely adopted and mixed into PEO matrix in order to facilitate the formation of localized amorphous regions and further promote the ionic transportation. Blending low molecular weight polyethylene glycol (PEG) with high molecular weight PEO was also demonstrated to be able to reduce the crystallized phase of the PEO matrix.[9] Recently, Chen and co-workers reported a novel PEO/Li⁺ system with nano-channels formed by α -cyclodextrin (α CD), where the PEO/Li⁺ pair was confined. The nano-channels in the PEO-Li⁺- α CD composite could provide pathways for the directional transportation of Li⁺, contributing to a high ionic conductivity even though the PEO matrix inside the composite was highly crystallized.[10]

Solid polymer electrolyte films made via LbL deposition exhibit high film uniformity, low degree of crystallinity and moderate ionic conductivity. Lowman *et al.* reported electrostatic linked poly(ethyleneimide) (PEI)/PAA LbL films, which showed high ionic conductivity after being treated with oligoethylene glycol dicarboxylic acid as plasticizer.[11] However, in electrostatic interaction driven LbL films, the species usually interact strongly with each other. Thus the chain mobility is relatively low, which is not favourable for ions transportation.[12] Delongchamp and coworker demonstrated the PEO/poly(acrylic acid) (PAA) LbL multilayer films fabricated by hydrogen bonding driven LbL self-assembly.[13] The film showed an ionic conductivity of around $10^{-9} \text{ S cm}^{-1}$ after being post-treated with 0.1 M lithium salt solution. However, post-treatment was required in these systems to achieve satisfactory ionic conductivity, which at the meantime, hindered the application of these kinds of SPE in integrated devices. Nyugen and coworkers demonstrated a novel PEI/PAA/PEO/PAA multilayers system, which combined both hydrogen bonding and electrostatic interaction and showed ionic conductivity of $10^{-5} \text{ S cm}^{-1}$ at room temperature.[14] Even though no post-treatment was applied, the tetralayer design extended the processing time of the LbL deposition process.

Taking the merits of the LbL technique and inspired by the design of PECs as building blocks, we aim at developing suitable polymeric complexes as building blocks and taking it as an effective way to fabricate SPE with high ionic conductivity. In this chapter, first we discussed the possibility to follow the PECs design which has been demonstrated in chapter 4 and fabricate hydrogen bonding polymeric complexes for LbL SPE layers. Then we developed supramolecular complexes PEG- α -cyclodextrin (α CD) and demonstrated a novel SPE layer fabricated by alternatively stacking PEG- α CD complex and PAA via hydrogen-bonding interaction. Cyclodextrins (CDs) are cyclic oligosaccharide consisting of different numbers of glucose units. CDs possess cyclic spatial structure and could form inclusion complex with a wide range of guest compounds via supramolecular interaction.[15-19] In order to limit the formation of crystallized phase in PEG matrix, amine group modified PEG was chosen to form inclusion complexes with α CD. In this supramolecular complexes, the α CD could form nano-channels on the PEG backbone for lithium ion transportation.[10] Furthermore, the large amount of hydroxyl groups carried by α CD played an important role on the formation as well as the properties of resultant LbL films. Growth behaviour, morphology, thermal and electrical properties of the PEG- α CD/PAA multilayer films

were systematically investigated, and further evaluation of the potential application of the multilayer films as SPE in an electrochromic device was conducted.

5.2 Experimental Methods

5.2.1 Polymeric complexes synthesis

Hydrogen bonded complexes synthesis

PAA-PEO complexes were prepared by adding 6 mL ($M_w \sim 20,000$, 2 mg mL^{-1} , $\text{pH}=2.85$) PEO solution into 30 mL PAA solution ($M_w \sim 100,000$, 2 mg mL^{-1} , $\text{pH}=2.85$) under mild stirring. The mixture turned to a turbid suspension after a while, indicating the formation of PAA-PEO complexes. Excessive stir would cause dissolution of the complexes and the solution would become transparent. Similarly, the PEO-PAA complex suspension was prepared by adding 3 mL PAA solution into 30 mL PEO solution under mild stirring. Both PAA-PEO and PEO-PAA complexes were under metastable state, and should be used for LbL deposition process right after preparation.

Supramolecular complexes synthesis

PEG- α CD solution was prepared by adding certain amount of α CD (depending on the ratio between ethylene glycol (EG) unit and α CD) into PEG-NH₂ solution (2 mg mL^{-1} , $\text{pH}=2.85$). The solution was stirred at 40 °C for 12 hours before being used for LbL assembly. PAA solution was prepared by diluting PAA concentrated solution using DI water. The final concentration was 2 mg mL^{-1} with $\text{pH}=2.85$.

5.2.2 Fabrication of hydrogen bonding based LbL film

Quartz slides and Si wafers were treated in piranha solution (1:3 mixture of 30% H₂O₂ and 98% H₂SO₄), heating at 80 °C for 20 mins. (Caution: Piranha solution reacts violently with organic material and should be handled carefully.) These substrates were dried with N₂ before being used for LbL assembly. Indium Tin Oxides (ITO) coated glass slides ($15 \text{ } \Omega \text{ sq}^{-1}$) were cleaned by 15 mins intervals of sonication in acetone, methanol and Milli-Q water. ITO-glass substrates were

treated with oxygen plasma for 2-3 mins in order to obtain a hydrophilic surface before being used for LbL assembly. The LbL deposition was performed using Carl Zeiss Model HMS70 slide stainer. The freshly cleaned substrates were first immersed into hydrogen donor solution for 10 mins, followed by being rinsed twice (2 mins each time) in pH-adjusted DI water bath. Then the substrates were immersed into hydrogen acceptor solution for 10 mins and rinsed in pH-adjusted DI water again, resulting in a bilayer film. The procedure was repeated n times to fabricate an n double-layer film. After assembly, the films were air-dried and then placed in humidity chamber under a 52% relative humidity. All the solutions used for LbL assembly contain 0.1 M LiClO_4 as lithium ion source.

5.2.3 Characterization

The formation of the inclusion complex was confirmed by ^1H NMR (Bruker Advance-500 NMR spectrometry, 500MHz). Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer Spectrum) was also used to analyse the interaction between PEG- NH_2 and αCD . QCM-D data was collected from a Q-Sense E4 instrument (Q-sense AB, Gothenburg, Sweden). Before test, the Au coated quartz plates (5 MHz) were treated by oxygen plasma for two mins. Morphology study was done on Field-emission Scanning Electron Microscopy (FESEM, JEOL 7600F). Sample roughness was recorded using Atomic Force Microscope (AFM) tapping mode with a DI 3100 (Veeco, Digital Instruments). Thickness of the films was measured using surface profiler and further reconfirmed with FESEM cross-section image. Fine structures of the LbL films were characterized by low voltage Transmission Electron Microscope (TEM, Carl Zeiss Libra 120 Plus). Ultraviolet-visible (UV-Vis) spectra were recorded on a UV-Vis spectrophotometer (Shimadzu UV3600). The thermal properties were studied by Thermal Gravimetric Analysis (TGA, Q500) and Modulated Differential Scanning Calorimeter (MDSC, TA Instruments 2920). The electrochemical impedance spectra (EIS) were recorded on Solartron 1470E, in the frequency range of 10 MHz to 0.01 Hz with the signal amplitude of 10-50 mV. The testing cells for electrochemical test consist of two ITO-coated glass slides placed in parallel and the LbL films sandwiched in between. The ionic conductivity was determined from fitted Nyquist plot. All the ionic conductivity values in this study were the average of 3 parallel sets of samples.

5.3 Results and Discussion

5.3.1 Dual polymeric complexes hydrogen-bonded LbL film

In Chapter 4, we designed sphere-like PECs for electrochromic active layer fabrication. The design was targeted at developing novel building blocks which could contribute to fast growth LbL films with porous structure. The sphere-like PECs possess relatively large dimensions with hydrophobic cores and hydrophilic shells. During the deposition process, there will be strong repulsion between the PECs due to the charge accumulation on the PECs, leading to a loosely packed structure. Inspired by this design, we first developed PEO-PAA and PAA-PEO complexes as building blocks and prepared [PEO-PAA/PAA-PEO]_n films for SPE application. We expected that by pre-engaging PEO and PAA into a complex, the interaction between PEO from the PEO-PAA complex and PAA from the PAA-PEO complex could be weakened by the steric effect of the complexes. Thus in the resultant PEO-PAA/PAA-PEO system, the mobility of PEO chains would be higher than that in the traditional PEO/PAA multilayer films, in which the PEO is highly restricted by the hydrogen-bonding interaction with PAA.

However, during the impedance test, we found that lithium salt easily crystallized on the film surface during the drying process. As shown in Figure 5.1, crystalline lithium salts could be easily recognized under optical microscopy. Even though 0.1 M lithium salts were added into every solution during the LbL deposition including the washing steps, it was to ensure that the lithium salts in the assembled LbL films would not diffuse into solution during the washing steps. Considering the high solubility of lithium salts in PEO matrix, this should not be an issue in PEO based films. It was suspected that due to the formation of polymeric complexes, the interaction between the PEO and PAA in the complexes occupied large amount of ether oxygen atoms and reduced the effective locus that could load lithium ions. Thus most of the lithium ions in PEO-PAA and PAA-PEO suspensions simply dissolved in water rather than interacted with PEO backbone. During the drying process, the water inside the LbL films was evaporated and the salts dissolved in the water migrated and crystallized on the film surface. Because ITO-coated glass slides instead of lithium block electrodes were used as electrodes in the impedance test, these crystallized salts not only indicated low lithium ions loading inside the film, but also greatly

interfered with the impedance results. Hence, this system was found out to be unsuitable for SPE application. Novel polymeric complex systems that could introduce candidates facilitating the lithium ions transportation, at the same time, without affecting the loading of lithium ions into the matrix was highly desirable as building blocks for LbL SPE fabrication.

Figure 5.1 Optical-microscopy images of a $[\text{PEO-PAA/PAA-PEO}]_{48}$ film surface with a magnification $100\times$. Lithium salts crystalline structures could be recognized clearly.

5.3.2 Layer-by-Layer deposition of supramolecular complexes PEO- α CD and PAA for SPE application

PEG- α CD inclusion complex formation and PEG- α CD/PAA LbL film fabrication

Based on the discussion in 5.3.1, we developed supramolecular complex PEG- α CD as a promising complementary building block with PAA for LbL SPE films fabrication. It has been reported that the α CD could provide pathway for lithium ions transportation along the PEO backbone and would not affect the loading of lithium ions into PEO matrix.[10] What's more, the steric effect of α CD could help to avoid strong interaction between PEG and PAA during LbL deposition, improving the chain mobility of PEG in the resultant films.

The schematic structure of PEG- α CD inclusion complex and the process of LbL deposition is shown in Figure 5.2. It is well known that α CD can form inclusion complex with low molecular weight PEG via host-guest interaction.[20] The complex formation was mainly driven by the hydrophobic-hydrophobic interaction between the cavity of α CD and the $-\text{CH}_2-\text{CH}_2\text{O}-$ units of PEG, as well as the hydrogen bond interaction between the PEG backbone and the hydroxyl groups

situated along the rim of α CD threaded onto the PEG chain.[21] In this work, we studied supramolecular complexes formed by amine group modified PEG (Mw=10,000, Sigma Aldrich) and α CD with three different ratios of EG unit to α CD (5:1, 10:1 and 15:1, which were denoted as PEG- α CD₅, PEG- α CD₁₀ and PEG- α CD₁₅, respectively). A lower ratio of EG unit to α CD, such as 3:1, resulted in precipitates instead of a stable complex solution.

Figure 5.2 Schematic structure of the PEG- α CD complex structure and the Layer-by-Layer assembly of PEG- α CD/PAA multilayer films.[22] Reproduced from Ref. 22 with permission from the American Chemical Society.

FTIR was employed to characterize the formation of the inclusion complex. The spectrum of PEG- α CD₁₅ in the region from 4000 cm⁻¹ to 500 cm⁻¹ was shown in Figure 5.3. The spectra of pure α CD and PEG-NH₂ were also recorded as reference. The characteristic bands of α CD were observed at 1028 cm⁻¹, 1078 cm⁻¹ and 1157 cm⁻¹, which were assigned to the coupled C-C/C-O stretching vibrations and the antisymmetric stretching vibration of the C-O-C bridges. The band at 2928 cm⁻¹ corresponded to the C-H stretching mode, and the band at 3394 cm⁻¹ was assigned as O-H stretching mode. All these bands could be identified in the spectrum of PEG- α CD complex. However, the band at 3394 cm⁻¹ in the spectrum of α CD was observed at lower frequency at 3367 cm⁻¹. This band shift indicated the formation of hydrogen bond between the ether groups on the included PEG chains and the hydroxyl groups on α CD.[16, 20]

Figure 5.3 FTIR spectra of pure α CD, PEG-NH₂ and PEG- α CD complex.[22] Reproduced from Ref. 22 with permission from the American Chemical Society.

The PEG- α CD complex formation was further confirmed by NMR. The chemical shifts of the inner protons of α CD (H3 and H5) in the PEG- α CD complex were recorded by ¹H NMR (D₂O) with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as an external reference. As shown in Figure 5.4, compared to pure α CD, the chemical shift of H3 of α CD in PEG- α CD₁₅ complex shifted from 3.978 to 3.976. The chemical shift of H5 of α CD shifted from 3.845 to 3.844. These phenomena suggest that PEG- α CD inclusion complex were formed successfully.[17]

Figure 5.4 (a) Chemical structure of α CD; (b) ¹H NMR spectra of PEG-NH₂, α CD and PEG- α CD₁₅ in D₂O.

The formation of PEG- α CD/PAA LbL film was mainly based on the hydrogen bonding between ether oxygen atoms on PEG backbone and carboxyl groups of protonated PAA. It is known that pH will affect the ionization degree of the carboxyl groups and the configuration of the PAA polymer chains to a great extent.[23] In general, pH of PAA solution below 3 is required for

establishing stable H-bond between PAA and the H-bond acceptor (which is PEG in our case).[24, 25] In this work, the pH of all the solutions were strictly kept at 2.85 in order to get a stable LbL system, as well as to avoid strong interaction between PAA and PEG, which is not beneficial to ion transportation.[26]

QCM-D was used to evaluate the deposition condition and monitor the film growth within the first 12 bilayers. As shown in Figure 5.5a, the adsorption of PEO- α CD and PAA could reach saturation within 5 mins, and the effect of DI washing vanished within 3 mins. These facts indicated that the deposition condition (10 mins for PEO- α CD solutions and PAA solutions) and washing condition (twice, 2 mins each) were appropriate for LbL film fabrication. The frequency changes during the first 12 deposition cycles were recorded in Figure 5.5b. It could be seen that during the first 12 deposition cycles, the film tended to follow exponential growth.

Figure 5.5 (a) Frequency change and Dissipation change obtained from QCM-D during the first bilayer deposition; (b) Frequency change extracted during the first 12 bilayers deposition.

Film growth was also represented by the change of film thickness recorded by surface profiler (Figure 5.6). It could be seen that the films with α CD were thicker than the film without α CD. As the deposition cycle increased, the thickness of PEG- α CD₁₅ film almost followed the linear growth; while the thickness of the PEG- α CD₅ and PEG- α CD₁₀ films showed retarded growth. These phenomenon could be explained as follows. Firstly, the α CD possesses special spatial structure. The existence of α CD in the films may contribute to loopy packed films compared to the α CD free PAA/PEG system, which resulted in thicker films. Secondly, as the α CD threaded on PEG are randomly distributed on PEG backbone, they could be considered as ‘defects’ for the multilayer construction. It could be deduced that certain amount of α CD could cause strong steric effect between different layers, leading to an unstable growth of film thickness as the deposition cycle

increases. The ‘defects’ would form more like a regular structure together with PEG when the amount of ‘defects’ increases, such as in the LbL film consisting of PEG- α CD₅, leading to a relatively steady growth of film thickness. Similarly, when the amount of ‘defects’ was reduced, the steric effect of the defects was not strong enough to influence the growth behaviour of the film distinctly. Thus in our case, the films with different ratios of α CD showed different growth behaviours. It should be noticed that QCM data revealed that the PEG- α CD₁₅/PAA film follows the exponential growth. While from the thickness change monitored by surface profiler, the growth of PEG- α CD₁₅/PAA film roughly followed the linear trend. The conflict of the two results could be attributed to the limitations the two characterization methods. The QCM-D could provide precise information on the change of the substrates surface. However, the tests were done on Au coated quartz plates, which were different from ITO coated glass substrates. While the surface profiler could only record the thickness of bulk film, of which the accuracy was not high.

Figure 5.6 Thickness of the LbL films versus deposition cycles.[22] Reproduced from Ref. 22 with permission from the American Chemical Society.

Figure 5.7 (a-c) Cross-session FESEM image of (a) [PEG- α CD₅/PAA]₄₈, (b) [PEG- α CD₁₀/PAA]₄₈ and (c) [PEG- α CD₁₅/PAA]₄₈ films; (d) Top-view FESEM image of a [PEG- α CD₁₅/PAA]₄₈ LbL film,[22] Reproduced from Ref. 22 with permission from the American Chemical Society.

Figure 5.8 (a-f) AFM images of [PEG-αCD₅/PAA]₄₈ (a-b), [PEG-αCD₁₀/PAA]₄₈ (c-d) and [PEG-αCD₁₅/PAA]₄₈ (e-f) films, respectively; (h) RMS extracted from AFM measurement of the LbL films.

The morphology of the LbL films was studied using FESEM and AFM. As shown in Figure 5.7, the multilayer films are continuous, possessing compact structure with a relatively smooth surface. Surface roughness was further characterized by AFM (Figure 5.8). Within a scanning area of 10 μm × 10 μm, the root mean square roughness values were all below 1.5 nm for the LbL films with different αCD ratio. AFM images also supported that all the LbL films possessed smooth surfaces.

Thermal Properties of PEG- α CD/PAA Multilayer Films

TGA Thermal properties of the LbL films were characterized by TGA and MDSC. TGA curves of pure PEG, PAA and α CD within the temperature range of 100-600 °C were shown in Figure 5.9a. Both PEG and α CD possessed single decomposition process, while multiple decomposition steps were observed for PAA. The weight loss before 130 °C stood for the loss of bound water in PAA matrix. The small step at 130-160 °C was referred to the release of water from intramolecular anhydride formation. The release of water from intermolecular anhydride formation was corresponding to the weight loss between 160-280 °C. Further weight loss resulted from decarboxylation and depolymerization can be recognized between 280-480 °C.^[27] Figure 5.9b showed the TGA curves of [PEG- α CD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ multilayer films. Both films demonstrated similar weight loss behavior. For [PEG/PAA]₄₈, the first main step started from 185 °C and ended at around 280 °C, with 19.4% weight loss. The second main step was around 285-470 °C, with 47.9% weight loss. For [PEG- α CD₁₅/PAA]₄₈, the first main weight loss showed up around 195-275 °C, which started at slightly higher temperature than that of [PEG/PAA]₄₈ film. The second main weight loss appeared at around 275-550 °C, with 66.9% weight loss. It was worth noting that the small amount of weight loss at around 130-160 °C assigned to the loss of water from intramolecular anhydride formation (as discussed above) was only observed in the [PEG/PAA]₄₈ film. It was attributed to the fact that the hydroxyl groups on the α CD rim could provide more opportunities to form hydrogen bonding with PAA than the part of PEG backbone α CD threaded on, thus the thermal stability (below 250 °C) of PAA in the LbL film with α CD was slightly improved.

Figure 5.9 TGA curves of (a) pure α CD, PAA and PEG-NH₂, and (b) [PEG- α CD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ multilayer films.[22] Reproduced from Ref. 22 with permission from the American Chemical Society.

Modulated-DSC (MDSC) MDSC curves of the first two measurement cycles of the LbL films were recorded in Figure 5.10. MDSC measurements were conducted from -25 °C to 100 °C in order to avoid film decomposition. There was no sharp endothermic peak associated with crystallized structures could be observed in any multilayer films, which indicated that the LbL films were dominated by amorphous phase. Glass-transition temperatures (T_g) of the LbL films with different ratios of α CD were determined from reversing heat flow of the first heating cycle. As shown in Figure.10, all the LbL films exhibited a single T_g , which laid between the reported T_g of pure PEG ($T_g \sim -60$ °C) and pure PAA ($T_g \sim 103$ °C),^[28, 29] The single T_g indicated these hydrogen-bonded LbL films were assembled homogeneously without obvious phase separation. Moreover, compared with other PEO based solid electrolyte systems fabricated via LbL technique, our films with α CD exhibit much lower T_g .^[26, 30, 31] The low T_g revealed that the polymer segment possess relatively high mobility even under room temperature, which was favorable for ion transfer in solid state polymer films. The α CD not only presents special spatial structure, but also possesses large amount of hydroxyl groups which could form hydrogen-bonding with PAA. It could be referred that the hydrogen-bonding between PAA and PEG was weakened by the competition effect and space steric effect from the existence of α CD. Thus both the PEG and PAA chains in PEG- α CD/PAA films were relatively more flexible than those in the PEG/PAA films, in accordance with the lower T_g . The selected area electron diffraction pattern recorded by low voltage TEM also reveals that the film is dominated by amorphous phase, which corroborates the X-ray diffraction pattern of the film (Figure 5.11). However, it should be noted that the whole film

was not absolutely amorphous. We did observe minute crystallized structures scattered on the film from low voltage TEM, which could result from the poor dissolution of high molecular weight PAA under low pH and high ionic strength condition. It was worth noting that among the LbL films with different ratios of α CD, PEG- α CD₁₅/PAA showed the lowest T_g around -13°C , while PEG- α CD₁₀/PAA possessed highest T_g . Taking the growth behavior of these three LbL systems into account, the higher T_g of PEG- α CD₁₀/PAA and PEG- α CD₅/PAA systems could be attributed to uneven distribution of PAA and PEG- α CD complex in the films. Especially for PEG- α CD₁₀/PAA system, the obvious retarded growth of film thickness indicates unequal absorption of PAA and PEG- α CD₁₀ among each deposition cycle, which was associated with uneven interaction between the building blocks. In contrast, the PEG- α CD₁₅/PAA system demonstrated a quite stable linear growth behavior, which suggested a well-balanced interaction between PEG and PAA as well as α CD and PAA, contributing to a uniform distribution of PAA and PEG- α CD₁₅ through the whole film. The MDSC results reveal that among the three LbL systems with α CD, the PEG- α CD₁₅ could show maximum contribution on lowering down the T_g .

Figure 5.10 MDSC data of (a) [PEG/PAA]₄₈ and [PEG- α CD₁₅/PAA]₄₈ films and (b) [PEG- α CD₅/PAA]₄₈ and [PEG- α CD₁₀/PAA]₄₈ films during the first heating cycle; (c) reversing heat flow curves

from -20 °C to 20 °C during the first heating cycle.[22] Reproduced from Ref. 22 with permission from the American Chemical Society.

Figure 5.11 (a) Low voltage TEM image of PEG- α CD₁₅/PAA multilayer film, and (b) the selected area electron diffraction pattern of the film. XRD pattern of [PEG/PAA]₄₈ and [PEG- α CD₁₅/PAA]₄₈ LbL multilayer films.

Electrical Properties of PEG- α CD/PAA Multilayer Films

Ionic conductivity of the LbL films under different relative humidity and temperatures were systematically analyzed. Firstly, the effects of α CD ratio and deposition cycles on ionic conductivity of LbL films were investigated (under RT, RH). As shown in Figure 5.12, the ionic conductivity increased with deposition cycles. Among the films with different ratios of α CD, the PEG- α CD₁₅/PAA system showed the highest ionic conductivity. The ionic conductivity values of the LbL films with 48 bilayers measured against temperature (298 K to 393 K) were shown in Figure 5.13. In general, the ionic conductivity values of the films with α CD were much higher than the films without α CD in the whole tested temperature range. Among the films with α CD,

the [PEG- α CD₁₅/PAA]₄₈ films presented the highest ionic conductivity of around $2.5 \times 10^{-5} \text{ S cm}^{-1}$ under room temperature, while the ionic conductivity of [PEG/PAA]₄₈ films was only around $5 \times 10^{-7} \text{ S cm}^{-1}$ under the same condition. For the films with α CD, the ionic conductivity first dropped around one order magnitude as the temperature increases from 298 K to 313 K due to the evaporation of remaining water inside the films. This phenomenon revealed that humidity was the dominating factor for ionic conductivity of the films with α CD below 313 K. Above 313 K, the films with different ratio of α CD showed different behaviors as the temperature further increases. For [PEG- α CD₁₅/PAA]₄₈ multilayer films and [PEG- α CD₁₀/PAA]₄₈ films, the ionic conductivity increased as the temperature rose from 313 K to around 345 K, after which the ionic conductivity of the films reached a plateau region of around $7 \times 10^{-5} \text{ S cm}^{-1}$ and $2.5 \times 10^{-5} \text{ S cm}^{-1}$ for [PEG- α CD₁₅/PAA]₄₈ and [PEG- α CD₁₀/PAA]₄₈, respectively. In the case of the [PEG- α CD₅/PAA]₄₈ films, the ionic conductivity of the films first jumped from $9 \times 10^{-7} \text{ S cm}^{-1}$ to around $7 \times 10^{-6} \text{ S cm}^{-1}$, when the temperature rose from 313 K to 323 K, and then slightly increased as the temperature increases from 323 K to 353 K. After that, the ionic conductivity reduced as the temperature further increased up to 400K, which could result from the loss of moisture inside the film as well as the loss of the bound water of PAA after 393 K. Unlike films with α CD, the ionic conductivity of LbL films without α CD did not decrease when the temperature increases from 298 K to 303 K. On the contrary, the ionic conductivity increased as the temperature rose from 303 K to 333 K, which revealed that temperature played a more important role than humidity on the ionic conductivity. After 333 K the ionic conductivity of the PEG/PAA films reached a plateau region up to 353 K, behaving similarly as the films with α CD. When the temperature was further raised to 383 K, the ionic conductivity of PEG/PAA films fluctuated between about $2 \times 10^{-6} \text{ S cm}^{-1}$ and $8 \times 10^{-6} \text{ S cm}^{-1}$. Our films showed competitive performance with the LPEI/PAA/PEO/PAA tetralayer system reported earlier, and the PEG- α CD₁₅/PAA system possessed even higher ionic conductivity under high temperature than the tetralayer system.[14]

Figure 5.12 Ionic conductivity of LbL films with different deposition cycles.

Compared to other SPE made via LbL self-assembly, our films containing α CD also expressed superior ability on ion transfer. For example, Hammond and co-worker reported a PEO/PAA multilayer film assembled from solutions containing 0.1 M lithium salt showed ionic conductivity only around 10^{-9} S cm⁻¹ under RT. The film could reach 10^{-5} S cm⁻¹ by post immersion in more concentrated lithium salt solution.[13] A porous LPEI/PAA multilayer system which possessed ionic conductivity around 6×10^{-9} S cm⁻¹ was also developed by their group. The performance of the porous film could be further improved by immersing it into a plasticizer solution. It could be seen that post treatment is required for all these system to facilitate the ion transfer in the LbL film. While in our study, we achieve fast ion transfer in LbL films simply by introducing supramolecular complex PEG- α CD as building blocks, without adopting any post treatment method. Several factors contribute to the higher ionic conductivity of the LbL films containing α CD: first of all, lithium salt has high dissolubility in PEG matrix. In our study, the deposition conditions are carefully modified, so that the PAA possesses proper protonation degree, which ensures the formation of multilayer films based on hydrogen bonding, in the meantime preventing strong interaction between PAA and PEG. Secondly, the spatial steric effect of α CD prevents compact stacking of PEG and PAA, thus the polymer chains have higher mobility. Moreover, the α CD threaded along the PEG chains could provide channels for Li⁺ ion transportation.[10]

Figure 5.13 (a) Ionic conductivity measured against temperature for: [PEG/PAA]₄₈ (black), [PEG-αCD₅/PAA]₄₈ (pink), [PEG-αCD₁₀/PAA]₄₈ (blue), and [PEG-αCD₁₅/PAA]₄₈ (red). (b) Ionic conductivity measured under different relative humidity for: [PEG/PAA]₄₈ (green) and [PEG-αCD₁₅/PAA]₄₈ (pink).[22] Reproduced from Ref. 22 with permission from the American Chemical Society.

The ionic conductivity of the [PEG-αCD₁₅/PAA]₄₈ films under different relative humidity was also investigated. The testing cell was placed in a humidity chamber under room temperature. When the sample was exposed a certain relative humidity, it should be stabilized for at least 24 hours before test. The [PEG-αCD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ films were firstly exposed to relative high humidity environment (100%RH), and then the humidity was lowered gradually (ionic conductivity values indicated by dots in Figure 5.13b). It could be observed that both [PEG-αCD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ reach their highest ionic conductivity under 100%RH, which were around 1.5×10^{-4} S cm⁻¹ and 1.5×10^{-6} S cm⁻¹, respectively. The ionic conductivity of the [PEG/PAA]₄₈ films decreased when the relative humidity of the environment was reduced because of the removal of the water inside the films. However, [PEG-αCD₁₅/PAA]₄₈ films almost retained the high ionic conductivity when the relative humidity of the environment was reduced. Even when the [PEG-αCD₁₅/PAA]₄₈ films were exposed to 30%RH, they still showed a relatively high ionic conductivity similar to the value when exposed to 100%RH. In order to investigate the reason for this unexpected phenomenon, the as-prepared testing cells containing [PEG-αCD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ were first stabilized under low relative humidity (30%RH), and then exposed to higher relative humidity environment (ionic conductivity values indicated by histogram in Figure 5.13b). Both kinds of films demonstrated increasing ionic conductivity values as the relative humidity of the environment was increased. This behaviour could be attributed to the increased moisture inside the films, which improved the mobility of the polymer chains. It was surprising

that after the [PEG- α CD₁₅/PAA]₄₈ films are exposed to 100%RH, the ionic conductivity would not decrease when the relative humidity was lowered again. These phenomena indicated that the [PEG- α CD₁₅/PAA]₄₈ films possessed high ability of water retention, which means that once the moisture was absorbed into the film, it was very difficult to extract the moisture by exposing the films under low relative humidity environment. It should be noticed that all the LbL films were tested between two parallel conductive electrodes, which may hinder the removal of water inside the films. However, both the [PEG- α CD₁₅/PAA]₄₈ films and [PEG/PAA]₄₈ films were investigated under similar conditions to ensure a fair comparison. The strong ability of water retention of [PEG- α CD₁₅/PAA]₄₈ was attributed to the large amount of hydroxyl groups on α CD, which could form hydrogen bonds with water molecules and help to confine the water molecules inside the multilayer films. It also provides an explanation for the fact that the humidity was the dominating factor for the films with α CD as the temperature increases from 303K to 333K, while the temperature is the dominating factor for the films without α CD. Comparison on ionic conductivity of the LbL films in this study and other similar LbL systems reported in the literature is shown in Table 5.1. It could be seen that the LbL SPE films with α CD studied in this work demonstrated high ionic conductivity without any post-treatment. Although there are reports of PEO based SPE prepared by other methods, such as blending with plasticizer or copolymerization, showing higher ionic conductivity above 10^{-4} S cm⁻¹ under ambient atmosphere,[32-34] the LbL self-assembly technique provide a facile method to directly form a thin and conformal coating on the demanded surface with control of film components and structure on molecular level. Moreover, there is no report of the water retention ability of the SPE as demonstrated in this study.

Mechanical durability study of the multilayer films was also conducted by monitoring the ionic conductivity before and after bending test of the LbL films, which were sandwiched between 2 pieces of cleaned ITO coated PET flexible substrates. The bending test was conducted for 100 cycles with a bend radius R=0.85cm. The ionic conductivity of the film was recorded every 5 bending cycles. As shown in Figure 5.14, the films could maintain an ionic conductivity higher than 2.0×10^{-6} S cm⁻¹ after 35 bends. The ionic conductivity dropped dramatically after 35 bends, which could result from delamination of the LbL polymer film from ITO-PET substrates, as well as loss of conductivity of ITO-PET substrates during bending test (the sheet resistance of the ITO-PET substrate increased from $3.8 \Omega \text{ sq}^{-1}$ to more than $3000 \Omega \text{ sq}^{-1}$ after 40 bends).

Table 5.1 Room Temperature (25 °C) of Ionic Conductivity of LbL films in this study compared to those reported in the literature

LbL SPE Films	σ (S cm ⁻¹)	Reference
PAH/PAA (pH 6.5/6.5)	3×10^{-9}	[35]
PAH/PSS (pH 3.5/3.5)	2×10^{-7} (90% RH)	[35]
LPEI/PAA (pH 5.0/5.0)	6.4×10^{-9} (52% RH) 1×10^{-5} (100% RH)	[36]
LPEI/PAA (pH 2.0/2.0)	5.6×10^{-10} (52% RH) 1.2×10^{-6} (100% RH)	[36]
LPEI/poly(2-acrylamido-2-methyl-1-1propanesulfonic acid) (PAMPS)	9.4×10^{-6} (52% RH, no salt) 1×10^{-5} (100% RH, no salt) 1.3×10^{-8} (52% RH, 0.2 M NaCl) 1.5×10^{-5} (100% RH, 0.2 M NaCl)	[36]
PEO/PAA	3×10^{-10} (52% RH) 5.5×10^{-5} (100% RH) 1.3×10^{-5} (52% RH, soaked in 1M LiCF ₃ SO ₃)	[13]
LPEI/PAA (pH 5.0/5.0)with oligoethylene glycol dicarboxylic acid treatment (pH 2.0)	9.5×10^{-5} (22% RH)	[11]
LPEI/PAA/PEO/PAA (PEO 20K)	4.8×10^{-5} (52%RH) 8.5×10^{-4} (100% RH)	[14]
LPEI/PAA/PEO/PAA (PEO 300K)	1.3×10^{-5} (52% RH) 1.7×10^{-4} (100% RH)	[14]
PEG- α CD ₁₅ /PAA in this study	2.5×10^{-5} (52% RH) 1.5×10^{-4} (100% RH)	[22]

Figure 5.14 Plots of ionic conductivity versus number of bending cycles of [PEG- α CD₁₅/PAA]₄₈ films.

Finally, in order to evaluate the availability of our LbL films functioning as a SPE layer, a functional electrochromic device was presented with WO₃ as active material and PEG- α CD₁₅/PAA multilayer film as solid polymer electrolyte. A 500 nm WO₃ film was deposited onto cleaned ITO-coated glass via electrochemical deposition. After that, a 24-bilayer PEG- α CD₁₅/PAA film was directly deposited onto the WO₃ layer, in order to have a good contact between the WO₃ layer and the SPE layer. Another cleaned ITO-coated glass was then pressed onto the LbL film as counter electrode. The device shows moderate optical modulation when switched between -2.5V and 0.5V, as shown in Figure 5.15. While under the same device fabrication method and test conditions, the device with a 24-bilayer PEG/PAA film as solid electrolyte did not show any color change because of the low ionic conductivity of the SPE layer. This functional device revealed that our method could effectively provide a continuous formation of solid electrolyte layer with high ionic conductivity that could support the ions transport during electrochemical reaction. However, further modifications on the LbL film were required to reduce the inner resistance of the device and improve the contact between the SPE and the electrochromic active layer.

Figure 5.15 Performance of an EC device with a [PEG- α CD/PAA]₂₄ LbL film as solid polymer electrolyte. Inset are the digital images of the EC device under bleached state and colored state.

5.4 Conclusions

In this chapter, we focused on developing suitable polymeric complexes as building blocks for LbL SPE fabrication. We first adopted the strategy that we used to develop PECs in chapter 4 and developed PAA-PEO/PEO-PAA system. However, further studies showed that this strategy was not suitable for SPE layers fabrication due to the poor lithium salt solubility and low ionic conductivity. To introduce species that could facilitate the ions transportation inside the Lbl film via polymeric complexes became the most promising strategy. Hence, we developed supramolecular complex PEG- α CD and successfully fabricated [PEG- α CD/PAA]_n multilayer films as SPE. We systematically studied the formation of the supramolecular complex, and analysed the growth behaviour, morphology, thermal properties as well as the ionic conductivity of the films with different α CD ratios. It has been found out that the existence of α CD played an important role in the film growth as well as the ionic conductivity of the LbL films. Compared to [PEG/PAA]_n films, the LbL films with α CD possessed lower T_g and higher ionic conductivity. Among all the LbL systems studied, the PEG- α CD₁₅/PAA films show the best performance with ionic conductivity of $2.5 \times 10^{-5} \text{ S cm}^{-1}$ under room temperature, and up to $7 \times 10^{-5} \text{ S cm}^{-1}$ under 345 K. The higher ionic conductivity of the films containing α CD was attributed to the presence of the channels for lithium ion transportation formed by the α CD threaded along the PEG chains as well as the loopy packing of PEG and PAA due to the steric effect of α CD, which contributed to the higher mobility of PEG chains. It is noteworthy that due to the large amount of hydroxyl groups on α CD, the [PEG- α CD₁₅/PAA]₄₈ films could hold the moisture inside the films when exposed under high RH, possessing high ionic conductivity, and maintain that high ionic conductivity even when the films were further placed under low humidity environment. This work demonstrated that with careful design of the complexes candidates, using polymeric complexes as building blocks is a facile and effective approach to introduce functional species into LbL films and develop SPE with high ionic conductivity for electrochemical devices.

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Chapter 6

Layer-by-Layer Deposition for Ag Nanowire based Transparent Conducting Film with Polymeric Capping Layer

For transparent electrochemical devices, such as electrochromic devices, the current collectors are required to be highly conductive as well as transparent in the visible light region. Traditional transparent conducting films (TCFs) are made from conducting inorganic oxide, which could not meet the requirements of flexible and stretchable devices. Metallic nanowire (NW) based networks, such as Ag NW network, possesses high conductivity and high transparency, holding the potential as conducting inorganic oxide substitution. Due to the requirement of charge complementary species with the conducting material, LbL technique does not show much advantages in the fabrication of highly conductive TCFs. However, taking advantages of the precise control of LbL self-assembly on each layer, LbL technique could be used for depositing capping layer for Ag NW based TCF, improving the conductivity and protecting it from oxidization without compromising transparency. In this chapter, conducting Ag NW networks with high transparency fabricated by LbL technique is presented. LbL coating of conductive polymeric complexes on the conducting network as a capping layer is developed, which further improves the conductivity as well as the stability of the films. The feasibility of adopting the LbL TCFs in electrochemical applications is evaluated as conducting substrates for electrochromic studies.

6.1 Introduction

Current collector is a key component for electrochemical devices. For some of the smart devices, such as electrochromic devices, low sheet resistance (normally lower than $50 \Omega \text{ sq}^{-1}$) and high transparency are required. Conducting inorganic oxides, such as indium doped tin oxide (ITO) and fluorine doped tin oxide (FTO), possess high transparency, high conductivity as well as good chemical stability. Thus they are the most classic and widely used transparent conducting electrode, adopted in various kinds of electronic and electrochemical devices. However, with the rapid development of flexible and stretchable devices, the brittle nature of the inorganic oxides and high temperature annealing process hinder their application in deformable devices. Novel transparent conducting films (TCFs) that could be easily processed on flexible or stretchable substrates are highly desired.

Several types of conducting materials have been exploited as substitutes for conducting inorganic oxide based electrodes, including conducting polymers such as PEDOT: PSS, carbon based conducting materials such as graphene and carbon nanotubes, as well as metallic nanowire (NW) networks. The sheet resistance of TCFs made from conducting polymers and carbon based materials is usually in a range of thousands to tens of ohms, which is relatively high for electrochemical applications. Moreover, surface modification or charge complementary species are required when introducing these materials into LbL deposition, which further lowers the conductivity of the resultant LbL film. Metallic NWs show high electronic conductivity and could deliver high transparency due to its subwavelength dimensions and the low loading amount on the substrates, thus attracting lots of interests. Ag NW is the most popular candidate because of its well-controlled preparation method. Several approaches have been demonstrated to form Ag NW network on various kinds of substrates, resulting in flexible or stretchable TCFs with high conductivity and high transparency. For example, the group of Cui fabricated Ag NW network on PET substrates via a facile solution process.[1] They studied the impacts of Ag NW aspect ratio as well as the galvanically replaced Au coating on the conductivity and transmittance of the resultant films. The TCF with Au coating could deliver $20 \Omega \text{ sq}^{-1}$ with transmittance of 80% (excluding the substrate) at 550nm. Lee and co-workers adopted roll-coating assisted LbL assembly to form Ag NW/PDDA multilayer film on PET substrates.[2] They pointed out that the

introduction of PDDA contributed to the homogeneous distribution of Ag NWs and helped to shield the surface charge of Ag NW (which was derived from the surfactant on the nanowires), thus reducing the electrostatic repulsion between Ag NWs and improving the contact between nanowires. A 5 bilayer Ag NW/PDDA film could deliver resistance of $10.6 \Omega \text{ sq}^{-1}$ with transmittance of 90% (excluding the substrate) at 550nm. Graphene oxide (GO) was also used as over-coating layer on the Ag NW multilayer films to improve the mechanical property of the conducting network. The films with GO coating also demonstrated excellent stability under ambient conditions and various chemical treatment, including exposure to H_2S gas and immersion in ethanol. However, for metallic NW based conducting network structure, normally the NWs only cover certain amount of the surface area of the substrates (less than 20%). The area that left empty between two NWs could be several μm^2 , which is insulating.[3] It is not beneficial for electrochemical applications, where effective charge injection/extraction within the whole contact area is required. Besides, the surface roughness of the metallic NW based TCF is relatively high because the diameters of the NWs are usually several tens of nanometers, hindering their application where smooth surface is demanded, such as organic thin film devices. Moreover, Ag NWs are easily oxidized in the presence of oxygen. Especially in electrochemical studies, Ag NWs suffer from severe oxidization and corrosion under positive potentials, hindering their application for most electrochemical applications.[4] One approach to solve these problem is to combine metallic NWs with conducting polymers, such as PEDOT: PSS. Considering the moderate conductivity and transparency of PEDOT: PSS, it is critical to control the amount of the PEDOT: PSS on the metallic NW network to ensure reduced surface roughness, without compromising the transparency and the conductivity of the whole film, in which case LbL deposition is a promising technique to realize so.

In this study, we adopted roll-coating LbL method to fabricate transparent and conducting multilayer Ag NW film. In order to reduce the surface roughness and improve the conductivity as well as the stability, PEDOT: PSS/PDDA multilayer films were deposited on top of the Ag NW network as capping layer. Morphology, topography, transparency and conductivity of the multilayer films were studied. The stability of the TCF with capping layer under ambient environment and under electrochemical test were also investigated.

6.2 Experimental Methods

6.2.1 Conducting film preparation

Ag NW network preparation

Conducting Ag NW network was prepared by roll-coating assisted LbL technique on polyethylene terephthalate (PET) substrates. Before deposition, PET substrates (12 cm × 8 cm) were cleaned by ethanol and DI water (Milli-Q, 18.2 Ω), and dried by N₂ flow. The substrates were subsequently treated by oxygen plasma for 3 mins. After that, the PET substrates were immediately immersed in poly(diallyldimethylammonium chloride) (PDDA) solution (high molecular weight, 2 mg mL⁻¹) for 15 mins, followed by rinsing in DI water for 3 mins. Commercial Ag NW suspension (XFNA_{no}, Ag NW L100) was diluted by isopropyl alcohol (IPA) and shook vigorously, with a final concentration of 0.5 mg mL⁻¹.

To prepare conducting Ag NW network, 0.5 mL diluted Ag NW suspension was first applied onto the PDDA modified PET substrates. Then, a uniform coating of Ag NW suspension was formed with the assistance of a machine-controlled Mayer rod (8#, with a moving speed of 20 mm s⁻¹). After the IPA was completely evaporated, the substrate was immersed in PDDA solution (1mg mL⁻¹) for 1 min, and subsequently washed by DI water for 1min. The film was dried under 60 °C to remove moisture. These steps were repeated n times, resulted in a (Ag NW/PDDA) _{n} conducting Ag NW network.

Formation of (PEDOT: PSS/PEI) _{n} LbL capping layer

Different from our previous work, in which the polymer complexes (PCs) were prepared by mixing two polymers under controlled conditions, PEDOT could not be easily dissolved in common solvents and form complexes with other polymers. Thus the PSS was selected to interact with PEDOT as a doping agent and charge balancing species during the polymerization of EDOT, resulting in a conducting PEDOT: PSS complexes which could be further processed into stable aqueous solutions. In this study, PEDOT: PSS complexes solution was prepared by diluting 2 mL commercial PEDOT: PSS (0.8 %wt in H₂O, conductive ink) with 18 mL pH adjusted DI water (pH=2), with a final concentration of 0.08 %wt. To form capping layers on the conducting Ag NW

network, 0.8 mL diluted PEDOT: PSS solution was applied on the Ag network, and spread out to form a uniform coating by a machine-controlled Mayer rod (8#, with a moving speed of 50 mm s⁻¹). After being dried under 60 °C, the film was washed by DI water for 1 min and dried again. Subsequently, the film was immersed in PDDA solution (1 mg mL⁻¹) for 1 min and washed with DI water for 1 min, followed by heating under 60 °C. These steps were repeated n times to form a [PEDOT:PSS/PDDA]_n over-coated layer on Ag NW network.

6.2.2 Characterization

Morphology study of the conducting layers was conducted on Field-emission Scanning Electron Microscopy (FESEM, JEOL 7600F). Topography and surface roughness were characterized using Atomic Force Microscope (AFM) tapping mode (Asylum Research Cypher S) with a scan area of 10 μm×10 μm. The transmittance of the conducting multilayer films was examined by a UV-Vis spectrophotometer (Shimadzu UV2700). Electronic conductivity was measured by a four point probe. All the conductivity values in this study were the average of 9 points of the examined sample. Electrochemical stability studies of the conducting LbL films were done in a 3 electrode test cell, with the conducting multilayer film as working electrode, a Ag/AgCl standard electrode as reference electrode and a Pt plate as counter electrode.

6.3 Results and Discussion

As discussed in 6.1, metallic NWs are promising materials to form transparent conducting electrode. In our study, we chose metallic Ag NWs with mean length of 200 μm and an average diameter of 100 nm. The Ag NWs were wrapped with poly(vinylpyrrolidone) (PVPON) and slightly negatively charged. Positively charged polyelectrolyte PDDA was employed as a bridging material to connect Ag NWs and PET substrates, as well as to shield the electrostatic repulsion between different layers of Ag NWs. Considering the geometric nature of Ag NW, electrostatic interaction will not be strong enough to provide firm interaction between Ag NWs and the substrates against gravity. Thus it is very hard to apply dip coating based LbL technique, where the substrates are vertically placed, to form a uniform coating of Ag nanowire on substrates. To solve this problem, we adopted roll coating- assisted LbL self-assembly to fabricate Ag NW

network on PET substrates. As shown in Figure 6.2a-c, Ag NWs were uniformly distributed on PET surface, forming an interconnected network structure. The density of Ag NWs on PET substrates increased upon deposition cycles. There were no obvious gaps between Ag NWs at the junctions (Figure 6.2d). PEDOT: PSS/PDDA capping layers were directly deposited on top of Ag NW network. It could be seen that polymeric coating was successfully formed on Ag NW surface. With 4 bilayers of PEDOT: PSS/PDDA over-coating, most of the Ag NWs were embedded in the polymeric film. It is worth noting that PEDOT: PSS/PDDA formed particles wrapping on the Ag NW junctions and decorating on the Ag NWs near the junctions. This phenomenon was not observed when a concentrated PEDOT: PSS solution was directly coated on the Ag NW network (as shown in Figure 6.2d). It was assumed that after the Ag NW/PDDA multilayer film deposition, the concentration of PDDA at the junctions was higher than that at the other parts of the network. As a consequence, during the LbL capping layer deposition, more PEDOT: PSS and PDDA were consecutively attracted at the junction, resulting in the formation of particles. EDS mapping of S distribution was shown in Figure 6.1h, revealing the full coverage of the whole area by PEDOT: PSS/PDDA.

Figure 6.1 Illustration of roll-coating assisted LbL deposition of TCFs.

Figure 6.2 FESEM images of (a-c) $[\text{Ag NW/PDDA}]_n$ multilayer films on the PET substrate with $n=1, 2, 4$, respectively; (d-f) $[\text{Ag NW/PDDA}]_4$ film with $[\text{PEDOT:PSS/PDDA}]_m$ capping layer with $m=1, 2, 3$, respectively; (g) EDS mapping of $[\text{Ag NW/PDDA}]_4$ - $[\text{PEDOT:PSS/PDDA}]_3$, indicating the distribution of S.

Surface topography of the $[\text{Ag NW/PDDA}]_4$ conducting films with different layers of $[\text{PEDOT:PSS/PDDA}]_m$ capping layer were monitored by AFM. The average diameter of Ag NWs used in this study is around 100 nm. It could be seen in Figure 6.3a that the height of Ag NWs on PET substrates was around 90 nm. After one and two bilayers PEDOT: PSS/PDDA coating, the height of Ag NWs on the substrates were measured to be 70-80nm and 50-60 nm, respectively. The height variation could be due to the non-uniformity of the Ag NW diameter (which could be revealed from Figure 6.3b), as well as the force exerted by the coated polymeric layer, compressing Ag NW network tightly to the substrates and leading to the reduction in height. After 3 bilayers PEDOT: PSS/PDDA coating, the height of most Ag NWs on substrates could be reduced to 30-40 nm. After being coated with PEDOT: PSS/PDDA LbL over-layer, the surface of the Ag NWs became rough and particles could be observed on the junction of Ag NWs and the PET substrates, which is consistent with the SEM observation.

Figure 6.3 AFM images and the selected line plots of (a) $[\text{Ag NW/PDDA}]_4$ film; (b-d) $[\text{Ag NW/PDDA}]_4\text{-}[\text{PEDOT:PSS/PDDA}]_n$ films with $n=1, 2, 3$, respectively.

The variations of transmittance of the $[\text{Ag NW/PDDA}]_n$ multilayer films with $[\text{PEDOT:PSS/PDDA}]_n$ capping layers were shown in Figure 6.4a. The transmittance discussed in this work represents for the specular transmittance, measured using UV-Vis spectrometer with air as reference, without using the integrated sphere. Under this test condition, the bare PET substrate possessed a transmittance around 88% from 450 nm to 850 nm. With the increase of Ag

NW/PDDA deposition cycles, the transmittance of the film slightly dropped. After 4 bilayers of Ag NW/PDDA coating, the film could still deliver a high transmittance within the visible light range. The transmittance at 550 nm of the multilayer films was extracted from Figure 6.4a and the corresponding sheet resistance of the films were shown in Figure 6.4b. Due to the low density of Ag NW on the PET substrate, the sheet resistance of the first 2 bilayers of Ag NW/PDDA films could not be measured by the four point probe. It could be seen that the sheet resistance of a three bilayer Ag NW/PDDA film was around $1200 \Omega \text{ sq}^{-1}$; while with the 4th bilayer Ag NW/PDDA coating, the sheet resistance was further reduced to around $150 \Omega \text{ sq}^{-1}$. After being over-coated with 3 bilayers of PEDOT: PSS/PDDA LbL film, the transmittance of the film at 550 nm decreased from 82% to 70%, with sheet resistance further reduced to $4 \Omega \text{ sq}^{-1}$.

The improvement on the conductivity was attributed to the conductive nature of PEDOT:PSS polymeric complexes and the continuous PEDOT:PSS/PDDA LbL coating on the Ag NWs network and the PET surface, providing charge carries between Ag NWs. What is more, the PEDOT: PSS/PDDA formed particles at the junction of Ag NWs, wrapping the Ag NWs and contributing to better connections between Ag NWs at the junctions. The charge transport in Ag NW based conducting film was mainly governed by the charge transport along the nanowires and the charge transport cross the junctions of the nanowires. The contact resistance at the Ag NW junction is proved to be a critical factor limiting the conductivity of the Ag NW based TCF.[1] One of the effective and widely adopted strategies to reduce the contact resistance at the nanowires junction is to ‘solder’ the nanowires together at the junction with metallic materials or semiconductors as media, such as Au and SnO_x . [3, 5] These media materials are formed in situ at the junctions, providing direct contact between Ag NWs or tightening the Ag together to provide a better connection. However, this approach is usually achieved by galvanic replacement or sol-gel process. Here we demonstrated that similar soldering structures could also be formed at the Ag NW junctions by LbL method. However, it could be noticed in Figure 6.2 and 6.3 that PEDOT: PSS/PDDA did not form particles at every junction, which indicated the poor controllability of our strategy. Further investigation and modification are required to improve the feasibility of adopting LbL technique to form the soldering structure on metallic NW network.

Figure 6.4 (a) UV-Vis spectra of the LbL TCFs; (b) Transmittance at 550 nm and sheet resistance of the LbL TCFs. The overcoating refers to PEDOT: PSS/PDDA on Ag NW network.

A digital photo of a scaled up TCF with a length around 12 cm and width around 8 cm was shown in Figure 6.5a. PET is well-known transparent plastic substrates with good flexibility. However, for the flexible films adopting PET as substrates, the mechanical stability and flexibility of the coating on PET is critical. Figure 6.5b presented the sheet resistance change after bending test with a bending radius of 0.5 cm. The sheet resistance of TCF without capping layer reached several $\text{M}\Omega$ after 300 cycles. For the TCF film with LbL capping layer, the sheet resistance did not show obvious change after 500 bending cycles, indicating good mechanical properties and flexibility of the TCFs with capping layer. Moreover, the TCF with capping layer could maintain conductivity after 3 times of scotch tape test (a piece of 3M scotch tape were attached to the samples surface and then peeled off); while for the TCF without capping layer, most of the Ag NWs in the test area were removed from the PET substrate after the scotch tape test and the film conductivity was lost. It is believed that the LbL overcoating layer helped to improve the mechanical stability of the TCF films by anchoring the Ag NWs on the PET substrates and improving the adhesion between the Ag NWs and the substrates.

Figure 6.5 (a) A digital photo of the $[Ag\ NW/PDDA]_4$ - $[PEDOT: PSS/PDDA]_2$ TCF film with a length around 12 cm and width around 8 cm; the resistance cross the diagonal line is 93.4 Ohm; (b). Sheet resistance change versus bending cycles (bending radius 0.5 cm).

Stability of the TCFs under ambient environment (temperature around 24.6 °C, humidity around 60%) was studied by monitoring the changes in sheet resistance within one month. As shown in Figure 6.6a, for $[Ag\ NW/PDDA]_4$ films, the sheet resistance was 40 times and 362 times higher than the original value after two weeks and three weeks, respectively. The sheet resistance could not be measured using four point probe after 4 weeks, indicating the aged film became insulating. However, for the films with $[PEDOT: PSS/PDDA]_3$ capping layer, the sheet resistance only increased to $121\ \Omega\ sq^{-1}$ after two weeks and could still maintain lower than $200\ \Omega\ sq^{-1}$ after 4 weeks. It is known that Ag NWs could be easily corroded in nanostructures.[6, 9] The improvement on the stability of the LbL TCF with capping layer compared to the bare Ag NW network under ambient environment was attributed to the good stability of PEDOT: PSS as well as the full coverage of network structure by the capping layer via LbL deposition. It was clearly showed in Figure 6.6 b-c that for the film without capping layer, silver NWs broke into shorter fragments and could not form a connected network structure after 4 weeks; while for the film with capping layer, the network structure was well maintained, indicating the Ag NWs were effectively protected from corrosion and degradation.. The degradation of Ag NWs in our work is revealed as a result of Ag NWs corrosion caused by the small amount of reducing sulphur-containing gases, such as H_2S and COS in the atmosphere, usually resulting in the formation of Ag_2S . The reaction of Ag corrosion caused by H_2S is believed to be:[6, 7]

The wrapping agent PVP on the Ag NWs surface help to adsorb water onto the Ag NWs, which acts as mediator for the change of Ag to Ag₂S. The existence of high moisture, oxygen and light under the ambient condition also facilitate and accelerate the corrosion of the Ag NWs.[8, 9] The existence of Ag₂S was confirmed by X-ray photoelectron spectroscopy (XPS) as shown in Figure 6.6d-e. The observed peaks from S 2p_{3/2} and S 2p_{1/2} electrons possess binding energy of 162.1 and 161.1 eV, respectively; while the peaks observed from Ag 3d_{5/2} and Ag 3d_{3/2} have binding energy of 368.2 and 374.2 respectively. These evidenced the formation of silver sulfide.[6] For the TCF with the LbL capping layer, the Ag NWs were prevented from H₂S and oxygen or water. Thus the network structure of Ag NWs was well kept intact, and the sheet resistance of the film remained almost the same much after 4 weeks.

Figure 6.6 (a) Stability of $[\text{Ag NW/PDDA}]_4$ and $[\text{Ag NW/PDDA}]_4\text{-}[\text{PEDOT:PSS/PDDA}]_3$ films under ambient conditions; (b) FESEM image of $[\text{Ag NW/PDDA}]_4$ films after 4 weeks under ambient conditions; (c) FESEM image of $[\text{Ag NW/PDDA}]_4\text{-}[\text{PEDOT:PSS/PDDA}]_3$ after 4 weeks under ambient conditions; (d) XPS spectra of S 2p_{3/2} and S 2p_{1/2} and e) XPS spectra of Ag 3d_{5/2} and Ag 3d_{3/2}.

One critical issue of Ag NW based TCF is the poor stability of Ag NW under electrochemical reactions. Ag NW could be easily oxidized under positive potential with presence of oxygen. Here we also investigated the electrochemical stability of our LbL Ag NW based TCFs. The $[\text{Ag NW/PDDA}]_4$ films and $[\text{Ag NW/PDDA}]_4\text{-}[\text{PEDOT:PSS/PDDA}]_3$ films were tested as working

electrodes under potential bias between -0.3 V to 0.2 V in 0.5 M KCl, 0.25 M H₂SO₄ and 0.5 M KOH, respectively. It is known that inorganic acid could become secondary doping to PEDOT: PSS. The small anions will penetrate into the PEDOT: PSS films and dope PEDOT instead of PSS, removing the insulating PSS from the PEDOT: PSS complexes. In this way, the distance between the conducting clusters is reduced, thus the conductivity of the PEDOT: PSS is high in acidic electrolyte.[10, 11] In the neutral electrolyte, the doping of PEDOT is mostly done by insulating PSS without any secondary doping. Hence, the conductivity of PEDOT: PSS is lower in neutral electrolyte than in the acidic electrolyte.[12] In the alkaline electrolyte, the PSS will be neutralized by the alkali and PEDOT will be dedoped, which results in significant increase on sheet resistance.[13] In our study, it was observed that for [Ag NW/PDDA]₄ films, the Ag NWs at the electrolyte /air interfaces were quickly oxidized and peeled off from PET substrates after 5 scan cycles in all the three electrolytes mentioned above. For the TCFs with [PEDOT: PSS/PDDA]₃ capping layers, the sheet resistance of the films did not change much after 50 cycles in the acidic electrolyte (as shown in Figure 6.7). In the neutral electrolyte, the sheet resistance slightly increased after 50 cycles because of the moderate conductivity of PEDOT: PSS. When tested in alkaline solutions, the TCF with LbL capping layer was destroyed and peeled off from the substrates after only 5 cycles due to the poor chemical stability (dedoping) of PEDOT: PSS. As mentioned above, the alkaline electrolyte will cause dedoping and phase separation between PEDOT and PSS. The removal of PSS will lead to aggregation of hydrophobic dedoped PEDOT and degradation of the continuous capping layer.[14] Thus no resistance results could be obtained for alkaline electrolyte. The improvement on electrochemical stability in acidic electrolyte revealed that our LbL [PEDOT: PSS/PDDA]₃ films fully covering Ag NW network could protect the Ag NW from being oxidized and acted as passivation layer effectively in proton based electrolyte.

Figure 6.7 (a) Stability of [Ag NW/PDDA]₄-[PEDOT: PSS/PDDA]₃ films after electrochemical test in 0.5 M KCl and 0.25 M H₂SO₄; The 1st and 50th CV curves of [Ag NW/PDDA]₄-[PEDOT: PSS/PDDA]₃ films in (b) 0.5 M KCl and (c) 0.25 M H₂SO₄, respectively.

In order to evaluate the feasibility of our TCFs as current collector in electrochemical devices, as well as to further demonstrate the advantages of adopting LbL PEDOT: PSS/PDDA capping layer, WO₃ films were directly deposited onto the TCFs as electrochromic active layer by electrochemical deposition (at -0.7 V for 300 s). From the FESEM images shown in Figure 6.8, it could be observed that for the TCF without capping layer, the WO₃ was deposited mostly on the Ag NWs and the film surface was rough. Cracks could be observed due to the non-uniform distribution of the stress in the thick WO₃ layer. However, for the TCF with LbL PEDOT: PSS/PDDA capping layer, the WO₃ uniformly covered the whole substrate and no cracks were observed, indicating conductivity improvement of the whole substrates as well as the lower surface roughness contributed by the PEDOT: PSS.

Figure 6.8 (a-b) FESEM images of WO_3 on $[\text{Ag NW/PDDA}]_4$ films; (c-d) FESEM images of WO_3 on $[\text{Ag NW/PDDA}]_4$ - $[\text{PEDOT: PSS/PDDA}]_3$ films.

Electrochromic properties of the WO_3 -TCF films were tested in 0.5 M H_2SO_4 with a Pt plate as counter electrode and the Ag/AgCl as the reference electrode. The UV-Vis spectra of the WO_3 -TCF films under 0 V and -0.8 V were recorded in Figure 6.9a. Considering the PEDOT: PSS could also show electrochromic activity under the testing conditions, the UV-Vis spectra of the TCF with capping layer were also recorded. It could be seen that for the WO_3 -TCF with capping layer, the contrast (ΔT , transmittance difference under colouring colored state and bleached state) at 630 nm was around $\Delta T = 22.6\%$, of which the PEDOT: PSS capping layer contributed around $\Delta T = 5\%$. However, under the same condition, the WO_3 -TCF without capping layer only showed $\Delta T = 9.4\%$. The larger coloration modulation was attributed to the more uniform deposition of WO_3 on the whole substrates of the TCF with capping layer as well as the improved conductivity contributed by the capping layer. Cycling stability was shown in Figure 6.9b. The films were switched under -0.8 V and 0 V with 30 s for each step. It could be observed that after 100 cycles, the contrast of WO_3 -TCF film without capping layer only remained around $\Delta T = 4.5\%$; while for the WO_3 -TCF film with PEDOT: PSS/PDDA capping layer, the contrast of the film could maintain $\Delta T = 15\%$ after 200 cycles. The improved cycling stability revealed that the capping layer could help to

prevent the Ag NW from being oxidized and degraded, maintaining good stability under electrochemical test. Switching times were described as 90% of the time taken for the completion of color conversion. For the WO_3 -TCF films without capping layer, the bleaching time was $T_b=5$ s and the coloration time was $T_c=16$ s. However, under the same testing condition, the WO_3 -TCF films with capping layer presented faster switching behavior with the bleaching time and coloration time of 5 s and 6 s, respectively. The improved kinetics of the electrochromic film on the TCF with capping layer demonstrated more effective charge transfer between the conducting substrates and the WO_3 layer with the presence of PEDOT: PSS/PDDA capping layer.

Under electrochemical test, the over-coated PEDOT: PSS layer could prevent Ag NWs from directly contacting oxygen and electrolyte. However, the electrolyte and oxygen could still penetrate into the polymeric capping layer slowly, which leads to oxidation of Ag NWs. Moreover, it is possible that Ag NWs could be oxidized by the oxidation state PEDOT: PSS during cycling test, although the PEDOT: PSS is not highly oxidized and possesses high oxidation ability within the tested potential window, facilitating the oxidization of Ag NWs and accelerating device failure. It is also worth noticing that after several tens of cycles, some of WO_3 and Ag NWs peeled off from the substrates. Especially for the substrates without the PEDOT: PSS/PDDA capping layer, the situation was even worse. It indicates that the poor interaction between oxidized Ag NWs and PET, as well as the poor interaction between oxidized Ag NWs and WO_3 layer, also give rise to the poor cycling stability of the EC devices. Further optimization of the capping layer is required to further improve the cycling performance of the EC devices.

Figure 6.9 Electrochromic properties of the WO₃-TCF films. (a) UV-Vis spectra of WO₃-TCF films under 0 V (straight line) and -0.8 V (dash line); (b) cycling stability of WO₃-TCF films switched between 0 V and -0.8 V at 630 nm; (c) transmittance versus time extracted from b for switching time calculation.

6.4 Conclusion

In this chapter, we presented our study on LbL Ag NW based TCF, as well as LbL capping layer with conducting polymeric complexes PEDOT: PSS. It was found out that by using LbL technique, the Ag NW could form a network structure and deliver high conductivity with high transparency. The sheet resistance of the TCF was further reduced by applying LbL PEDOT: PSS/PDDA capping layer. The transmittance and the resistance of the whole conducting layer can be systematically controlled by altering the deposition cycle of capping layer based on the different requirements of the practical application. Thus by adopting LbL approach, the features of the resultant TCF could be facily modulated according to the requirement of practical applications. Polymeric particles wrapping at the Ag NW junctions were formed during alternatively assembling PEDOT: PSS and PDDA on top of Ag NW network, which further improved the conductivity by

reducing the contact resistance at the Ag NW junction. Moreover, the over-coated PEDOT: PSS/PDDA acted as passivation layer, protecting Ag NW from being oxidized. Thus the stability of the LbL Ag NW TCF under ambient condition as well as in acidic and neutral electrolytes was improved. Considering the basic requirement of LbL technique that charge complementary species are needed between the conducting materials, LbL technique was not desirable for fabrication of TCFs with high conductivity and high transparency. The feasibility of adopting our TCFs in electrochemical applications was further exploited as the conducting substrates for an electrochromic layer. It has been demonstrated that with the LbL polymeric capping layer, the WO_3 could be deposited more uniformly on the substrates. Compared to WO_3 -TCF films without capping layer, the WO_3 -TCF films with capping layer showed enhanced electrochromism as well as electrochemical stability. Even though LbL self-assembly possess inherent drawbacks on forming transparent conducting layer, our study demonstrated that the conductive polymers, which are not able to participate in LbL process alone, could be introduced into LbL films in complexes form and make contributions to the formation of stable TCFs.

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Chapter 7

Summary and Future Work

In this thesis, innovative designs on PCs have been exploited to develop suitable building blocks for LbL electrochemical active layer, SPE layer, as well as transparent conductive layer, aiming to overcome the difficulties of traditional LbL technique on electrochemical device applications. This chapter presents a general discussion of our achievements accompanied by the reflection of the implications. Our insights and suggestions on further exploiting the potential of LbL technique on electrochemical device applications are also provided as future work.

7.1 Summary

This thesis is devoted to addressing the limitations of traditional LbL self-assembly on electrochemical studies, and exploiting PCs as LbL building blocks for electrochemical applications as a novel approach to overcome the remaining challenges. We focus on developing suitable types of PCs for the fabrication of three basic components in an electrochemical device, namely, the electrochemical active layer, SPE layer, and transparent conductive layer. The approaches to achieve the target were discussed starting from the analysis of the existing challenges and the initial design of the PCs, moving to the modification of the selected PCs or configuration of the PCs, followed by the systematic characterization and analysis of the resultant LbL films. Specific descriptions, achievements and reflections of our work are discussed in the following sections.

7.1.1 PCs as LbL building blocks for electrochemical active layer fabrication

LbL self-assembly has been demonstrated to be a very versatile method for thin film fabrication. The adoption of this technique on functional films preparation gained great success during the decades of development. However, the limitations of traditional LbL deposition on electrochemical applications are also notable. On one hand, LbL technique is criticized for its low efficiency on film fabrication. Only limited amount of materials could be deposited into the film within each deposition cycle, thus it will take hours even days to obtain a thin film with sufficient active material.[1] On the other hand, the compact structure of the traditional LbL films using individual polymers as building blocks impeded the redox reaction of the active materials inside the films.[2] These issues hinder the further development of LbL on electrochemical field and effective solutions are desired. PECs are promising candidates to fabricate fast growth LbL films with porous structure because of their large dimensions and charge accumulation on the complexes surface.[3] Aiming at develop PECs as building blocks to overcome the drawbacks of traditional LbL films, we developed dual PECs system PSS-PANI/PEI-PSS with PANI as the electrochromic active materials. The resultant films showed expected porous structure with fast growth behaviour, while the electrochemical activity of the film was poor. Considering the intrinsic insulating feature of the polyelectrolytes, how to maintain the electrochemical activity of the PANI became the main

concern of engaging PECs into the LbL films. Thus this system was evolved into mono PEC system PANI/PSS-PEI to ensure the active material inside the film was electrochemically accessible, and the composition of the PEC was further modified to a dual weak polyelectrolytes complex PAA-PEI in order to facilitate the redox reaction of PANI. Compared with traditional PANI/PAA film, PANI/PAA-PEI LbL films presented fast growth behaviour, special structures and enhanced electrochromism, benefiting from the presence of PEC as building blocks.[4] Noting that the basic mechanism of electrochromism is the electrochemical reaction of the active materials, with careful design and control of the PEC composition, adoption of this strategy is not limited to electrochromic films and could be expanded to the fabrication LbL films for all kinds of electrochemical applications.

However, there are some precautions for using PECs as building blocks. Firstly, the PEC should be a relatively uniform and stable system. The PECs in the solution should be able to maintain their composition and configuration during the whole LbL deposition process. Secondly, the repulsion between the PECs is relatively strong due to the charge accumulation on the PECs surface. This feature usually contributes to a LbL film with porous structure when PECs are used as building blocks, while at the same time, will leads to a discontinuous film at the first several deposition cycles.[5] Thus this strategy is not suitable for ultrathin conformal coatings. The fabrication of free standing films with high mechanical properties by this strategy is also not realistic. Thirdly, during the evaluation of the electrochromic properties of our films, we noticed that the cycling stability of our films was not satisfactory. After several tens of cycles, the films slightly dissolved into the liquid electrolyte and the optical modulation of the films decreased. As it is mentioned in Chapter 2, during the LbL self-assembly process, each layer will interact with the adjacent several layers and eventually form a stable film. It was suspected that when PECs were used as building blocks in our studies, the interaction between the adjacent layers was not as strong as it is in the films formed by individual polymers due to the steric effect of the PEC and the repulsion between the PECs. It should be also noticed that even though PAA-PEI, as a dual weak polyelectrolyte complexes, could act as proton carriers and facilitate the redox reaction of PANI, the PAA itself is not considered as the preferred doping agent for PANI as sulfonate acid possess strong interaction with PANI and could effectively protect PANI from over-oxidation during redox reaction. Further modification and regulation of the PEC compositions is required to

improve the stability of the resultant LbL films. Using solid electrolytes instead of liquid electrolytes is considered as another approach to avoid the dissolution of LbL films.

In conclusion, using PECs as building blocks is a facile method to fabricate electrochemical active LbL films with fast growth behaviour and porous structure that is favourable for electrochemical reactions, overcoming the limitations of traditional LbL technique. Careful design and control of the PECs are required to ensure the electrochemical activity as well as the stability of the LbL films.

7.1.2 PCs as LbL building blocks for SPE layer fabrication

SPE layer, as an ionic conductive layer communicating the electrochemical reactions on the anode and cathode, is an important element in an electrochemical device and has different requirements on the film structure and functionality with electrochemical active layers. The most apparent issue for SPE layer fabricated by LbL self-assembly is the low ionic conductivity that could hardly meet the requirement of a functional electrochemical device. The ionic conductivity of a polymer film is determined by the amount of free ions as well as the ion mobility, which is dominated by the mobility of chain segments.[6] Especially for LbL films driven by electrostatic interaction, the strong paired layers leads to limited number of free ions and poor ion mobility inside the films.[7] Targeting at improving the polymer chain mobility, we firstly develop hydrogen bonded PC as building blocks for LbL SPE layer based on the hypothesis that the steric effect of sphere-like PCs would weaken the interaction between the building blocks, thus the polymer chains would be less confined. However, our preliminary study of the designed PAA-PEO/PEO-PAA system revealed poor lithium salt solubility in this system. Thus we developed a novel PC, the supramolecular complex PEG- α CD formed by PEG main chain threading through the cavity of α CD, as a promising building block for SPE. We systematically studied the contribution of α CD on the formation of LbL films with PAA as complementary building block, and the thermal and electrical properties of the resultant films. Due to the special spatial structure of α CD, the LbL films with optimized ratio of α CD showed lower glass transition temperature and higher ionic conductivity compared with traditional PEG/PAA multilayer films. Moreover, the hydroxyl groups carried by α CD led to LbL films with high water retention. Once the films were exposed to high moisture,

the films could maintain high ionic conductivity even when it was transferred into very low humidity environment.[8]

When comparing the strategies used for fabricating the electrochemical active layer and the SPE layer, the importance of developing suitable PCs as building blocks with required functionality is highlighted. For the electrochemical active layer discussed in Chapter 4, porous films with fast growth behaviour are favourable for electrochemical reaction, thus sphere-like PECs with charge accumulation are suitable candidates as building blocks. Nevertheless, for the SPE layer discussed in Chapter 5, it is essential to improve the chain mobility of the matrix and promote the ion transportation inside the film. Hence, supramolecular complexes with α CDs, whose cavities possess steric effect and provide pathway for lithium ions, are better choices than sphere-like PCs. It could be seen that the key to develop suitable building blocks for functional LbL films is to understand the dominating factor contributing to the functionality. The diversity of the composition and structure of PCs provide more feasibility and flexibility on the design of building blocks. Thus PCs possess great advantages towards individual polymers as building blocks for functional LbL films.

7.1.3 Conducting PCs for TCF capping layer fabrication

When it comes to the TCF fabrication, we first considered the limitations of LbL technique on this application. To form a multilayer film, LbL self-assembly requires charge complementary species for conducting materials, which are normally insulating. Thus LbL technique possesses limited advantages on fabricating TCFs with high conductivity. Taking merits of the precise control of LbL technique on each deposition layer, we focused our study on adopting LbL self-assembly on fabricating conducting capping layer on Ag NW networks. As a conventional conducting polymer, PEDOT possess high conductivity upon doping with acid and high transparency in visible light region. However, PEDOT itself could not dissolve in common solvents. Conducting polymeric complexes PEDOT: PSS, formed in the polymerization process of EDOT with presence of PSS, could be easily dispersed in aqueous solution. In our work, we adopted PEDOT: PSS and PDDA as building blocks for LbL capping layer on LbL Ag NW networks. The conducting PEDOT: PSS not only filled in the insulating area between the NWs, providing more charge carriers, but also

promoted the connection between NWs at the junctions, resulting in improved conductivity. The advantages of using LbL technique lies in the control of amount of PEDOT: PSS, thus the resultant TCF could deliver a low sheet resistance without sacrificing the transparency. The capping layer also protect Ag NW from being oxidized by oxygen under ambient condition as well as in neutral and acidic electrolytes with a small positive potential bias. Our work reveals that LbL technique could make its contribution on improving the properties of metallic NW based TCFs.

It should be pointed out that good connection between the Ag NW networks and the substrates is a key factor for the successful deposition of the LbL capping layer. In our work, the reason for adoption of roll-coating assisted LbL for Ag NW network formation was mainly about the geometry of Ag NWs, which were long and ‘heavier’ than traditional LbL building blocks. However, we still adopted roll-coating rather than dip coating process for polymeric capping layer preparation due to the fact that the interaction between the Ag NWs and substrates was not strong enough to bear the multiple dipping process in the dip coating LbL process. The surface tension of the solutions could remove the Ag NWs from the substrates during the LbL process, leading to a non-uniform and non-conductive film. Thus besides choosing suitable building blocks, the appropriate approach is also important for a stable LbL film formation.

7.2 Future Work

7.2.1 PCs as building blocks for Electrolyte-Free Electrochromic Device

Redox-active ionic liquids and liquid crystals have drawn great attention during the past decades.[9, 10] A redox-active ionic liquid or liquid crystal is an anisotropic material that possesses both electrochemical active moieties and ionic moieties, thus could present electrochemical activities without adopting any external electrolyte.[11, 12] These materials are expected to contribute to an electrolyte-free electrochemical device, simplifying the structure of the device and overcoming any non-compatibility in a device caused by the electrolyte. An example of electrochromic liquid crystal is shown in Figure 7.1. The liquid crystal consists of a π -conjugated moiety and an ionic conductive group and could self-assemble into a highly organized structure. Upon applying voltage, the ionic conductive group could help to form the electric double layer near the electrode, and

holes would be injected into the π -conjugated moiety, resulting in redox-reaction associated with changes on optical properties.[13] After being fabricated into a solid device, this material could exhibit electrochromism in bulk crystalline phase without any electrolyte. Another example is the electrochromic ionic liquid formed by modifying an ionic liquid with a viologen moiety (Figure 7.2). Similarly, the viologen moiety could be doped or dedoped by the counterions transported by the ionic liquid bonded to the viologen molecule and exhibit colour changes.[11]

Figure 7.1 a) Schematic image of the dual functional liquid crystal; b) photographs of a liquid crystal cell under different bias.[13] Reproduced from Ref. 13 with permission from the American Chemical Society.

Figure 7.2 Schematic of the redox reaction of the viologen-ionic liquid and associated colour change.[11] Reproduced from Ref. 11 with permission from the American Chemical Society.

Even though these systems are of great interests, redox-active ionic liquids and liquid crystals require complicated molecular design and synthesis. A facile approach to achieve the electrolyte-free system is desirable. Noting the advantages of PCs on integrating materials with different functionalities and the capability of LbL self-assembly on modulating interactions on molecular level, employing LbL technique with PCs as building blocks is a promising strategy to realize electrolyte-free electrochemical devices. PCs possess both electrochemical activity and ionic conductivity could be formed by combining an electrochemical active material with an ion hosted polymer. For example, PANI as an electrochromic material could interact with PEO via hydrogen bonding interaction, which could host and transfer lithium ions, and form PANI-PEO complex. With careful control of the candidates and configuration of these PC, the ionic conductive polymer in the PC should be able to provide ions for the adjacent electrochemical active materials in the PC during the redox reaction, achieving a non-electrolyte system. These multifunctional PCs could be further used for LbL self-assembly with a suitable complementary species and processed into a thin film used in electrochromic devices.

Figure 7.3 A schematic of the formation of multifunctional PCs and the resultant LbL film.

7.2.2 bL Fabrication of a Full Solid Electrochromic Device

Even though intensive studies have been done on fabricating functional LbL films, most of these LbL films employed in an electrochemical device are demonstrated as a specific part of the device, such as the electrochromic layer or a conducting layer. To adopt LbL technique to fabricate different layers in a sequence which could together form a full electrochemical device is very challenging, yet worth pursuing. The proposed fabrication process of an all LbL solid

electrochromic device is illustrated in Figure 7.4. Firstly, the conducting sublayer will be formed with LbL pattern on a substrate. Then the electrochromic active sublayer will be deposited directly on conducting sublayer via LbL self-assembly, followed by the deposition of SPE sublayer onto this electrochromic active layer. The electrochromic complementary layer will be subsequently deposited. Finally, ion storage sublayer and another LbL conducting sublayer fabricated on the top of this multilayer structure will result in an integrated film which could function as an independent electrochromic device. Since all the sublayers are formed via LbL assembly and interacted with each other, it is all about interfacial architecture, rather than simply packing different layers together. The difficulty of this strategy lies on regulating the compatibility of the deposition conditions of different functional sublayers, as well as the interfacial connection between different functional sublayers. For example, the electrochromic active layer should be stable under the deposition condition of the SPE layer, rather than decompose or dissolve in the solutions or onto electrochromic layer during the fabrication of SPE. Besides, the building blocks used in fabricating the previous layer should be able to interact with the building blocks of the latter layer, in order to guarantee the eventual formation of a steady LbL. If the interaction between different sublayer is poor, the latter layer could not be formed because the substratum of this sublayer is not stable. Considering the superiority of PCs on materials integration, it is expected that the advantages of adopting PCs as building blocks will be further unveiled. For those materials which could not interact directly with each other at the interface, employing them into PCs with other materials which possess more accessible sites will be a promising solution. It should be noticed that it is not feasible to simply combining the electrochromic active layer, SPE layer and TCF layer demonstrated in this thesis into a full solid device because of the electrochemical instability of Ag NWs within the working potential window of PANI. What is more, adopting PECs as building blocks could contribute to the formation of films with porous structure, which is favourable for liquid electrolyte diffusion. Nevertheless, when combined with the solid electrolyte, the contribution of porous structure to the redox reaction will not be as significant as in liquid electrolyte system. Thus novel PCs should be developed as building blocks for electrochemical active layer in order to exhibit superior performance in solid device. Self-doping PCs which are proposed in 7.2.1 will also be promising candidates for fabricating active layers in solid electrochemical device. We believe that realizing a full device fabricated by LbL self-assembly

will light up a new approach for device fabrication, and will also be illuminating for other bottom-up fabrication methods, such as inkjet printing and 3D printing.[14-16]

Figure 7.4 A schematic of the fabrication of an integrated film fabricated by LbL self-assembly.

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APPENDIX

Table A.1 Materials used in the thesis.

Materials	Quality	Supplier	Product number
poly(ethylenimine)	Mw=25,000	Polysciences	23966
poly (acrylic acid)	partially salted, Mw=5000, 50 wt% in solution	Aldrich Chemical	19203-1
poly(sodium-4-styrenesulfonate)	Mw ca. 70,000	Sigma-Aldrich	243051
polyaniline	emeraldine base, Mw ca. 5000	Sigma-Aldrich	556459
poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)	0.8 wt% in solution, conductive inkjet ink	Sigma-Aldrich	739316
N,N-Dimethylformamide	anhydrous, 99.8%	Sigma-Aldrich	227056
lithium perchlorate	>95.0% (Titration by AgNO ₃)	Sigma-Aldrich	205281
propylene carbonate	anhydrous, 99.7% purity	Sigma-Aldrich	310328
methoxypolyethylene glycol amine	10,000	Sigma-Aldrich	07965
α-cyclodextrin	>98%	Sigma-Aldrich	C4642
poly(acrylic acid)	average Mw~100,000, 35 wt.% in water	Sigma-Aldrich	523925
Ag NW	Ave. diameter: 100 nm Ave. length: >200 μ m	XFNANO	L100
Poly(diallyldimethylammonium chloride)	20 wt% in water	Sigma-Aldrich	409014