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Solid Polymer Electrolyte with High Ionic Conductivity via Layer-by-Layer Deposition

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ABSTRACT: A novel multilayer system via layer-by-layer (LbL) self-assembly by alternatively packing polyethylene glycol (PEG)- α -cyclodextrin (α CD) complex and poly(acrylic acid) (PAA) via hydrogen-bonding is designed and investigated in this work. The PEG- α CD inclusion complex is obtained by supramolecular interaction. Multilayer films with different ratios of α CD are fabricated, and the growth behavior, morphology, thermal properties and electrical properties of the resultant LbL films are systematically characterized. The films with PEG- α CD complex and PAA as building blocks show high ionic conductivity reaching up to $2.5 \times 10^{-5} \text{ S cm}^{-1}$ under room temperature (52%RH), which is almost two orders magnitude higher than the PEG/PAA films under the same conditions. The PEG- α CD₁₅/PAA films also possess high water retention due to the large amount of hydroxyl groups carried by α CD, which enables the films, after exposed to a high humidity environment, to maintain a high ionic conductivity under low humidity environment. This PEG- α CD/PAA LbL system provides an insight for designing polymer based solid state electrolyte and its application towards electrochemical devices.

INTRODUCTION

Solid polymer electrolyte (SPE) films possess high ionic conductivity and low electronic conductivity; high chemical, thermal and electrochemical stability, as well as robust mechanical properties.^{1,2} Compared to the liquid and gel electrolyte, SPE could provide wider electrochemical operation window, wider range of working temperature, easier processing and less corrosion issue of the electrodes. These features make SPE promising candidates for all-solid-state electrochemical device applications, such as lithium-ion batteries, fuel cells, sensors, dye-sensitive solar cells, electrochromic displays, smart windows, and flexible devices.

First discovered in 1973 and demonstrated in all-solid-state film battery in 1979, poly(ethylene oxide) (PEO)/Li⁺ system is one of the most classic and widely used systems for SPE because of the high solubility of Lithium salt in PEO matrix.³⁻⁵ It is known that the ion transport in the SPE is mostly dominated by the local relaxation and Brownian motion (segment motion) of the polymer chains, which are believed to be more favorable in the amorphous phase of the host polymer.² However, PEO easily forms the crystalline phase at room temperature (RT), which hinders its applicability where high ionic conductivity at RT is desired. Many approaches have been explored to improve the performance of PEO/Li⁺ SPEs. Inorganic fillers⁶ and organic plasticizers⁷ are widely introduced into PEO matrix in order to promote the formation of localized amorphous regions and further enhance the ionic transportation. Blending low molecular

weight polyethylene glycol (PEG) with high molecular weight PEO is another way to decrease the crystallinity of polymer matrix.⁸ Recently, Chen *et al.* demonstrated a novel PEO/Li⁺ system with nano-channels formed by α -cyclodextrin (α CD), in which the PEO/Li⁺ pair is confined. The nano-channels provide the pathway for the directional transportation of Li⁺ and, thus the PEO-Li⁺- α CD composite showed high ionic conductivity even though the PEO matrix is highly crystallized.⁹

Layer-by-Layer (LbL) self-assembly has been proven to be a powerful technique to fabricate thin films with integration of different components as well as functionalities.¹⁰⁻¹⁷ Solid polymer electrolyte films made via LbL deposition showed great film uniformity, low degree of crystallinity and high ionic conductivity under high humid environment. Delongchamp and coworker demonstrated the fabrication PEO/poly(acrylic acid) (PAA) LbL multilayer films driven by hydrogen bonding. After exposed to 0.1 M lithium salt solution, the film showed an ionic conductivity of around $10^{-9} \text{ S cm}^{-1}$.¹⁸ Soon after that, Lowman *et al.* reported electrostatic linked poly(ethyleneimide) (PEI)/PAA LbL films, which showed high ionic conductivity after treated with oligoethylene glycol dicarboxylic acid as plasticizer under low pH.¹⁹ However, post-treatment was necessary in these systems to obtain satisfactory ionic conductivity inside the films, which at the same time, will limit the application of these kinds of SPE in integrated devices. Nyugen *et al.* presented a novel PEI/PAA/PEO/PAA multilayers system, which combined both hydrogen bonding and electrostatic

interaction. Taking advantage of the high mobility of PEI chains, the PEI/PAA/PEO/PAA layers showed ionic conductivity of 10^{-5} S cm^{-1} at room temperature.²⁰ Even though no post-treatment was applied, the tetralayer design will extend the processing time of the LbL deposition process.

Taking the merits of the LbL technique and aiming at developing an effective way to fabricate SPE with high ionic conductivity, here we demonstrate a novel solid polymer electrolyte film fabricated by alternatively stacking PEG- α CD complex and PAA via hydrogen-bonding interaction. PEG, chemically synonymous with PEO, refers to oligomers and polymers with low molecular weight (<20000). The mobility of PEG chains are much higher than PEO due to the shorter polymer chains. However, the shorter polymer chains also indicates that PEG could form the crystalline phase much easier, which is unfavourable for SPE.² The cyclodextrin (CD) is a group of carbohydrates consisting of different numbers of glucose units. CDs are cyclic molecules which can form inclusion complex with a wide range of guest compounds via supramolecular interaction.²¹⁻²⁵ In this work, we selected an amine group modified PEG to form inclusion complexes with α CD. This complex was further used for LbL self-assembly with high molecular weight PAA. The amine terminal groups could help to limit the formation of the crystallized phase in PEG matrix, and the α CD could form nano-channels on the PEG backbone for lithium ion transportation. Furthermore, the large amount of hydroxyl groups carried by α CD play an important role on the formation as well as the properties of resultant LbL films. We systematically studied the growth behaviour, morphology, thermal and electrical properties of the PEG- α CD/PAA multilayer films, and further evaluated their potential application as SPE in an electrochromic device.

EXPERIMENTAL SECTION

Materials. Methoxypolyethylene glycol amine (PEG-NH₂, 10,000), α -cyclodextrin ($\geq 98\%$), poly(acrylic acid) solution (average Mw~100,000, 35 wt.% in water), and lithium perchlorate ($\geq 95\%$) were purchased from Sigma-Aldrich. All the chemicals were used as received. Milli-Q 18 M Ω water was used for all experiments. pH of all aqueous solutions was adjusted using diluted hydrochloric acid (0.1 M) and sodium hydroxide solutions (0.1 M).

LbL assembly of multilayer films. 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, pH=2.85). The solution was stirred at 40 °C for 12 hours before 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. DI water baths were adjusted to pH=2.85. All the solutions for LbL assembly contain 0.1 M LiClO₄ as Lithium ion source.

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 stored in Milli-Q water, and were dried with N₂ before used for LbL assembly. 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 with oxygen plasma for 2-3 mins in order to obtain a hydrophilic surface. The layer-by-Layer deposition was performed using Carl Zeiss Model HMS70 slide stainer. To fabricate PEG- α CD/PAA multilayer films, the freshly cleaned substrates were first immersed into PEG- α CD solution for 10 mins, followed by rinsing twice (each time for 2 mins) in pH-adjusted DI water bath. Then the substrates were immersed into PAA solution for 10 mins and rinsed in pH-adjusted DI water again, resulting in a bilayer film. The procedure was repeated to 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.

Characterization. The formation of the complex was confirmed by Fourier Transform Infrared spectroscopy (FTIR, Perkin Elmer Spectrum). NMR spectra were recorded on Bruker Avance-500 NMR spectrometry (500 MHz). QCM-D data was collected from a Q-Sense E4 instrument (Q-sense AB, Gothenburg, Sweden). The morphology and the thickness of multilayer films were characterized and determined by field-emission scanning electron microscopy (FESEM, JEOL 7600F). Sample roughness was measured using Atomic Force Microscope (AFM) tapping mode with a DI 3100 (Veeco, Digital Instruments). Surface profiler was also used to measure the thickness and the roughness of the multilayer films. 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 recorded on Thermal Gravimetric Analysis (TGA, Q500) and Modulated Differential Scanning Calorimeter (MDSC, TA Instruments 2920). The electrochemical impedance spectrum (EIS) tests were conducted 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 consist of two ITO-coated glass slides placed in parallel and the LbL films sandwiched in between. The ionic conductivity is determined from fitted Nyquist plot. All the ionic conductivity values in this paper are an average of 3 parallel sets of samples.

RESULTS AND DISCUSSION

1. Formation of PEG- α CD Complex and Layer-by-Layer Deposition of PEG- α CD/PAA Multilayer Films

Figure 1. Schematic structure of the PEG- α CD complex structure and the Layer-by-Layer deposition process of PEG- α CD/PAA multilayer films.

Figure 1 shows the schematic structure of PEG- α CD inclusion complex and the process of LbL deposition. The complex formation is driven by the 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.²⁶ The complex formation was confirmed by FTIR. As shown in Figure 2, the spectra of pure α CD and PEG in the region from 4000 cm^{-1} to 500 cm^{-1} were recorded for reference. The spectrum of α CD shows bands at 1028 cm^{-1} , 1078 cm^{-1} and 1157 cm^{-1} , which correspond 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} is assigned to the C-H stretching mode, and the band at 3394 cm^{-1} is recognized as O-H stretching mode.

Figure 2. FTIR spectra of pure α CD, PEG- NH_2 and PEG- α CD complex.

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 shifts to lower frequency at 3367 cm^{-1} , indicating the formation of hydrogen bond between hydroxyl groups on α CD and ether groups on the included PEG chains.^{22, 27} It is also observed that in ^1H NMR spectra, the chemical shifts of inner protons of α CD in PEG- α CD deviated from their original positions (Figure S1, supporting information). These evidence confirms that the PEG- α CD inclusion complexes have been formed successfully.

The deposition of the PEG- α CD/PAA multilayers was driven by the hydrogen bonding between carboxyl groups of protonated PAA and ether oxygen atoms on PEG backbone. It is known that the ionization degree of carboxyl groups and the configuration of PAA is highly dependent on pH.²⁸ In general, pH of PAA solution below 3 is re-

Figure 3. (a) Thickness of the LbL films versus deposition cycles, (b) Top-view FESEM image of a $[\text{PEG-}\alpha\text{CD}_{15}/\text{PAA}]_{48}$ LbL film, (c) cross-section FESEM image of a $[\text{PEG-}\alpha\text{CD}_{15}/\text{PAA}]_{48}$ LbL film, and (d) AFM topography image of a $[\text{PEG-}\alpha\text{CD}_{15}/\text{PAA}]_{48}$ LbL film.

quired for establishing stable H-bond between PAA and the H-bond acceptor (in our case it is PEG).^{29, 30} In this study, we strictly kept the pH of all the solutions to 2.85 in order to get a stable LbL system as well as to avoid strong interaction between PAA and PEG, which is not favourable for ion transportation.³¹ PEG- α CD complexes with three different ratios of EG unit to α CD (5:1, 10:1 and 15:1, which are denoted as PEG- α CD₅, PEG- α CD₁₀ and PEG- α CD₁₅, respectively) were used to fabricate multilayer films with PAA. A lower ratio of EG unit to α CD, such as 3:1, resulted in precipitates of the complex rather than a stable complex solution. Film growth was represented by the change of thickness characterized by surface profiler. QCM-D was also used to monitor the film growth (Figure S2, supporting information). As shown in Figure 3a, the thickness of PEG- α CD₁₅ film almost keeps the linear growth behaviour as the deposition cycle increases; while both the PEG- α CD₅ and PEG- α CD₁₀ films show retarded growth of the film thickness. Considering the spatial structure of α CD, the existence of α CD may contribute to loopy packed films compared to the α CD free PAA/PEG system. Thus the films with α CD are thicker than the film without α CD. The α CD threaded on PEG could be considered as 'defects' for the multilayer construction, as they are randomly distributed on PEG backbone. It could be deduced that certain amount of α CD could cause strong steric effect between different layers, which results in an unstable growth on film thickness as the deposition cycle increases. When the amount of 'defects' increases, such as in the LbL system consisting of PEG- α CD₅, the 'defects' will form more like a regular structure together with PEG, leading to a relatively steady growth on film thickness. Similarly, when the amount of 'defects' is reduced, the steric effect of the defects is not strong enough to have distinct influence on film growth. Thus in our case, the films with different ratios of α CD showed different growth behaviours.

The morphology of the LbL films was studied using FESEM and AFM. Figure 3b and 3c shows the top view FESEM image and the cross-section image of a [PEG- α CD₁₅/PAA]₄₈ multilayer film, respectively. It could be seen that the film is a continuous film which possesses compact structure with a relatively smooth surface. Other

films with PEG- α CD₅ and PEG- α CD₁₀ also show similar morphology (Figure S3, supporting information). Surface roughness was further studied by AFM. Figure 3d shows the AFM topography image of [PEG- α CD₁₅/PAA]₄₈ films. AFM images with larger scan area are also provided in the Supporting Information (Figure S4). It could be seen that these LbL films possess smooth surface.

2. 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 are shown in Figure 4a. Both PEG and α CD possess single decomposition process, while multiple decomposition steps are observed for PAA. The weight loss before 130 °C is referred to the loss of bound water in PAA matrix. The small step at 130-160 °C stands for the release of water from intramolecular anhydride formation. After that, water from intermolecular anhydride formation was released, which is corresponding to the weight loss between 160-280 °C. Further weight loss resulted from decarboxylation and depolymerization can be found between 280-480 °C.³² The TGA curves of [PEG- α CD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ multilayer films are shown in Fig. 4b. Both films show similar weight loss process. For [PEG/PAA]₄₈, the first main step starts from 185 °C and ends at around 280 °C, with 19.4% weight loss. The second main step is around 285-470 °C, with 47.9% weight loss. For [PEG- α CD₁₅/PAA]₄₈, the first main weight loss appears around 195-275 °C, which starts at slightly higher temperature than that of [PEG/PAA]₄₈ film. The second main weight loss shows up at around 275-550 °C, with 66.9% weight loss. The less percentage of residue from [PEG- α CD₁₅/PAA]₄₈ film results from the existence of α CD. However, the small amount of weight loss at around 130-160 °C assigned to the loss of water from intramolecular anhydride formation as discussed in Figure 4a, is only observed in [PEG/PAA]₄₈. It is supposed 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 of PAA component in the LbL film is slightly improved.

Figure 4. TGA curves of (a) pure α CD, PAA and PEG-NH₂, and (b) [PEG- α CD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ multilayer films.

Modulated-DSC (MDSC) MDSC curves of the first two measurement cycles of the LbL films were recorded (Figure S5, supporting information). To avoid decomposition of the LbL films, MDSC measurements were conducted from -25°C to 100°C . No sharp endothermic peak associated with crystallized structures can be observed in any multilayer films, which indicates that the LbL films were dominated by amorphous phase. Glass-transition temperatures (T_g) of the LbL films with different ratios of αCD were determined from reversing heat flow of the first heating cycle (Figure 5). All the LbL films exhibit a single T_g , which lies between the reported T_g of pure PEG ($T_g \sim -60^{\circ}\text{C}$) and pure PAA ($T_g \sim 103^{\circ}\text{C}$),^{33, 34} indicating these hydrogen-bonded LbL films were homogeneous assembled without obvious phase separation. Moreover, compared to other PEO based solid electrolyte systems fabricated via LbL technique, our films with αCD possess much lower T_g .^{31, 35, 36} The low T_g indicates a relatively high mobility of the polymer segment even under room temperature, which is beneficial to ion transfer in solid state polymer films. The αCD possesses special spatial structure, and the hydroxyl groups on the αCD could also form hydrogen-bonding with PAA. It can be referred that the hydrogen-bonding between PAA and PEG is weakened by the competition effect and space steric effect from the existence of αCD . Thus both the PEG and PAA chains in PEG- αCD /PAA films are relatively more flexible than those in the PEG/PAA films, in accordance with a lower T_g . The selected area electron diffraction pattern recorded by low voltage TEM (Figure S6, supporting information) also shows that the film is dominated by amorphous phase, which corroborates the X-ray diffraction pattern of the film (Figure S7, supporting information). However, it should be noted that the whole film is 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. This issue could be optimized by replacing the high molecular weight PAA with lower molecular weight ones or further adjusting the film fabrication conditions. It is

Figure 5. Modulated DSC curves for LbL films: reversing heat flow from -20°C to 20°C during the first heating cycle.

worth to note that among the three kinds of LbL films with different ratios of αCD , PEG- αCD_{15} /PAA shows the lowest T_g around -13°C , while PEG- αCD_{10} /PAA and PEG- αCD_5 /PAA films show higher T_g around 5.5°C and 1.4°C , respectively. Considering the growth behavior of these three LbL systems, the higher T_g of PEG- αCD_{10} /PAA and PEG- αCD_5 /PAA systems could result from uneven distribution of PAA and PEG- αCD complex in the films. Especially for PEG- αCD_{10} /PAA system, the obvious retarded growth on film thickness indicates unequal absorption of PAA and PEG- αCD_{10} within each deposition cycle, which associates with uneven interaction between polymers and αCD . In contrast, the PEG- αCD_{15} /PAA system shows a quite stable linear growth behavior, which suggests a well-balanced interaction between PEG and PAA as well as αCD and PAA, resulting in a uniform distribution of PAA and PEG- αCD_{15} through the whole film. The MDSC results show that among the three LbL systems with αCD , in PEG- αCD_{15} /PAA system, the αCD could show maximum contribution on lowering down the T_g .

3. Electrical Properties of PEG- αCD /PAA Multilayer Films

Electrical performance of the LbL films was studied under different relative humidity and temperatures. Firstly, the ionic conductivity of LbL films with different deposition cycles and amounts of αCD were investigated. For all LbL films with αCD , the ionic conductivity increases while increasing the number of deposition cycles (Figure S8, supporting information). The ionic conductivity values of the LbL films with 48 bilayers measured against temperature are shown in Figure 6a. In general, the ionic conductivity values of the films with αCD are much higher than the films without αCD in the whole tested temperature range. Among the films with αCD , the $[\text{PEG-}\alpha\text{CD}_{15}/\text{PAA}]_{48}$ films show the highest ionic conductivity of around $2.5 \times 10^{-5} \text{ S cm}^{-1}$ under room temperature, while the ionic conductivity of $[\text{PEG}/\text{PAA}]_{48}$ films is only around $5 \times 10^{-7} \text{ S cm}^{-1}$ under the same condition. For the films with αCD , the ionic conductivity first drops around one order magnitude as the temperature increases from 293K to 313K due to the evaporation of remaining water inside the films. It could be deduced that humidity is the dominated factor for ionic conductivity of the films with αCD below 313K. Above 313K, the films with different ratio of αCD show different behaviors as the temperature further increases. For $[\text{PEG-}\alpha\text{CD}_{15}/\text{PAA}]_{48}$ multilayer films and $[\text{PEG-}\alpha\text{CD}_{10}/\text{PAA}]_{48}$ films, the ionic conductivity increases as the temperature increases from 313K to around 345K, after which the ionic conductivity of the films reaches a plateau region of around $7 \times 10^{-5} \text{ S cm}^{-1}$ for $[\text{PEG-}\alpha\text{CD}_{15}/\text{PAA}]_{48}$ and $2.5 \times 10^{-5} \text{ S cm}^{-1}$ for $[\text{PEG-}\alpha\text{CD}_{10}/\text{PAA}]_{48}$. In the case of the $[\text{PEG-}\alpha\text{CD}_5/\text{PAA}]_{48}$ films, the ionic conductivity of the films first jumps from $9 \times 10^{-7} \text{ S cm}^{-1}$ to around $7 \times 10^{-6} \text{ S cm}^{-1}$, as the temperature rises from 313K to 323K, and then slightly increases as the temperature increases from 323K to 353K. After that, the ionic conductivity reduced as the

Figure 6. (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).

temperature further increases up to 400K, which could result from the loss of moisture inside the film as well as the removal of constitution water of PAA after 393K. Unlike films with αCD, the ionic conductivity of LbL films without αCD does not show any decrease at the beginning of temperature raise. On the contrary, the ionic conductivity increases as the temperature rose from 303K to 333K, which revealed that the temperature plays a more important role than humidity on the ionic conductivity. After 333K the ionic conductivity of the PEG/PAA films reached a plateau region up to 353K, behaving similarly as the films with αCD. When the temperature was further raised to 383K, the ionic conductivity of PEG/PAA films fluctuated between about 2×10^{-6} S cm⁻¹ and 8×10^{-6} S cm⁻¹. Our result is competitive with the LPEI/PAA/PEO/PAA tetralayer system reported earlier, and the PEG-αCD₁₅/PAA system possesses even higher ionic conductivity under high temperature than the tetralayer system.²⁰ Compared to other SPE made via LbL self-assembly, our films containing αCD also show superior performance on ionic conductivity. 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.¹⁸ They also developed a porous LPEI/PAA multilayer system which possessed ionic conductivity around 6×10^{-9} S cm⁻¹. The performance of the film could be improved by immersing it into a plasticizer solution. All these systems require post treatment to facilitate the ion transfer in the LbL film. While in our study, we achieve fast ion transfer in LbL films simply by introducing PEG-αCD complex as building blocks, without adopting any post treatment method. The higher ionic conductivity of the LbL films containing αCD can be attributed to the following reasons: first of all, PEG has high lithium salt dissolubility. Under the modified deposition conditions, PAA possesses proper protonation degree, which ensures the formation of multilayer films based on hydrogen bonding, at the same time preventing strong interaction between PAA

and PEG. Secondly, the spatial steric effect of αCD in the LbL films could also help avoid compact stacking of PEG and PAA, thus the polymer chains have higher mobility. Moreover, the αCD threaded along the PEG chains could provide channels for Li⁺ ion transportation.⁹ The ionic conductivity of the LbL films under different relative humidity was also investigated. The testing cell was placed in a humidity chamber under room temperature. The relative humidity inside the chamber was controlled and the sample was stabilized when exposed to a certain relative humidity for at least 24 hours before test. The [PEG-αCD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ films were first exposed to relative high humidity environment (100%RH), and then the humidity was lowered gradually (ionic conductivity values indicated by dots in Figure 6b). It could be seen that both [PEG-αCD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ reach their highest ionic conductivity under 100%RH, which are 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 decreases when the relative humidity of the environment is reduced, which was resulted from the removal of the water inside the films. However, the ionic conductivity of [PEG-αCD₁₅/PAA]₄₈ films does not change much when the relative humidity of the environment is reduced. Even when the films are exposed to 30%RH, the [PEG-αCD₁₅/PAA]₄₈ still shows 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 [PEG-αCD₁₅/PAA]₄₈ and [PEG/PAA]₄₈ testing cells 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 6b). Both kinds of films show increasing ionic conductivity values as the relative humidity of the environment is increased. This behaviour could be assigned to the increased moisture inside the films, which improves the mobility of the polymer chains. It is surprising that after the [PEG-αCD₁₅/PAA]₄₈ films are exposed to 100%RH, the ionic conductivity would not decrease when the relative

humidity is lowered again. These phenomena indicate that the [PEG- α CD₁₅/PAA]₄₈ films possess high ability of water retention, which means that once the moisture is absorbed into the film, it is very hard to extract the moisture by exposing the films under low relative humidity environment. It should be noticed that all the LbL films were sandwiched between two parallel conductive electrodes for electrical test, 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 tested under similar conditions to ensure a fair comparison. The strong ability of water retention of [PEG- α CD₁₅/PAA]₄₈ is attributed to the large amount of hydroxyl groups on α CD, which could form hydrogen bonds with water molecules and lock the water molecules inside the multilayer films. It also provides an explanation for the fact that the humidity is the dominated factor for the films with α CD as the temperature increases from 303K to 333K, while temperature is the dominated factor for the films without α CD. 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 flexible substrates. A functional electrochromic device is presented with WO₃ as active material and PEG- α CD₁₅/PAA multilayer film as solid polymer electrolyte (Figure S9&S10, supporting information).

CONCLUSION

Here we presented a new kind of LbL multilayer film consisting of PEG- α CD complex and PAA as building blocks. The PEG- α CD inclusion complex was successfully formed based on supramolecular interaction and used for LbL deposition. We studied the morphology, film growth behavior, thermal properties as well as the ionic conductivity of the films in order to evaluate their potential application as solid polymer electrolyte layers. The PEG- α CD complexes with different ratio between EG unit and α CD are successfully obtained and characterized by FTIR. MDSC curves show that the films are dominated by amorphous phase. When compared to PEG/PAA films, all the films with α CD show higher ionic conductivity within the temperature range 293K-393K. As the temperature increases, the ionic conductivity of PEG/PAA films is mostly controlled by temperature, while the ionic conductivity of the films with α CD is dominated by the moisture inside the film and temperature. Among all the LbL systems studied, the PEG- α CD₁₅/PAA films show the best performance with ionic conductivity of 2.5×10^{-5} S cm⁻¹ under room temperature, and up to 7×10^{-5} S cm⁻¹ under 345K. The higher ionic conductivity of the films containing α CD is attributed to loopy packing of PEG and PAA due to the steric effect of α CD, which leads to the higher mobility of PEG chains, as well as the presence of the channels for lithium ion transportation formed by the α CD threaded along the PEG chains. An even higher ionic conductivity of 1.5×10^{-4} S cm⁻¹ could be obtained from [PEG- α CD₁₅/PAA]₄₈ when they were exposed to 100%RH. It is

noteworthy that the [PEG- α CD₁₅/PAA]₄₈ films also show good water retention due to the large amount of hydroxyl groups on α CD, which leads to high ionic conductivity even at low RH. Once the films are exposed to high moisture environment, the films could hold the moisture inside the films, possessing high ionic conductivity, and maintain that high ionic conductivity even when the films are further placed under low humidity environment. We believe that our approach, which combine the supramolecular chemistry and LbL self-assembly, is a facile and effective method, to prepare solid polymer electrolyte layers with high ionic conductivity for electrochemical devices, such as electrochromic devices and supercapacitors.

ASSOCIATED CONTENT

Supporting Information. ¹H NMR spectra of PEG- α CD₁₅ complex, QCM-D data of first 12 deposition cycles, FESEM images of PEG- α CD₅/PAA and PEG- α CD₁₀/PAA films, AFM measurement of PEG- α CD₅/PAA, PEG- α CD₁₀/PAA and PEG- α CD₁₅/PAA films, MDSC data for LbL films, low voltage TEM image of PEG- α CD₁₅/PAA film, XRD pattern of PEG/PAA and PEG- α CD₁₅/PAA film, ionic conductivity of LbL films with different deposition cycles, mechanical bending test of PEG- α CD₁₅/PAA film, UV-Vis spectra of a functional EC device with PEG- α CD₁₅/PAA as SPE layer.

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