NOVEL CONJUGATED POLYMER PREPARED BY ELECTROCHEMICAL POLYMERIZATION AS ACTIVE MATERIAL IN SUPERCAPACITOR

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NOVEL CONJUGATED POLYMER PREPARED BY ELECTROCHEMICAL POLYMERIZATION AS ACTIVE MATERIAL IN SUPERCAPACITOR

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ABSTRACT

Electrochemical energy storage devices such as supercapacitors and batteries have attracted more and more attentions in recent years with the emerging of new materials and understanding of their properties\textsuperscript{1}. As one type of supercapacitors, Pseudocapacitor based on the redox-polymer provide additional pseudocapacitance compared to traditional electrostatic supercapacitors. They can enhance the specific capacitance and reduce the cost of the capacitor devices.\textsuperscript{2}

In this study, a novel bithiophene modified conjugated monomers were directly polymerized by electrochemical polymerization on the ITO glass substrate. The multiple thiophene units in polymers can undergo reversible redox reactions which is promising to provide additional pseudocapacitance. Furthermore, an activation phenomenon was investigated after polymerization, the areal based capacitance can be enhanced more than hundred times during activation. The asymmetric polymer-CNT supercapacitor device was fabricated and exhibited a great cycling performance, 85\% initial capacitance after 10000 cycles. In addition, flexible electrodes such as aluminum foil based substrate was used to replace ITO due to the convenience in device fabrication.
ACKNOWLEDGEMENTS

Firstly, the chance of doing research in Dr. Yu Zhu’s group and advices from him is greatly appreciated for me. In addition, thanks Dr. Stephen Z.D. Cheng for spending his valuable time on my thesis. It’s my honor to invite you as my master thesis reader.

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CHAPTER I

INTRODUCTION AND BACKGROUND

1.1 Supercapacitor

Electricity is important for the development of modern society, however, the electricity generated source is unlike other type of Energy source like fossil oil or coal, which can be mined and stored or transfer to energy, when electricity is generated, it must be used immediately or need to converted to another type of energy such as chemical or potential. Typically people storage electricity into two types of devices, capacitors and batteries. Battery can storage large amount of electricity and capacitor can storage and release electricity in fast rate, this two type of devices are indispensable in modern electric devices.

In recently years, a new type of energy storage device is investigated, supercapacitor as one type of electrochemical energy storage devices gain its popularity due to the advantage of high power density and long cycle time compare to traditional capacitor. Based on the capacitance source, Supercapacitor can be classified into Electrostatic Double Layer Capacitor (EDLC) and Pseudocapacitor. The EDLC is made by two carbon electrode which can get electrostatic storage by the separation of charge in Helmholtz double layer
at the interface between the electrode surface and electrolyte. A typical EDLC is showed
in fig 1.1. The whole device is constructed with two carbon based electrodes and separated
by one piece of separator, two current collectors are connected to each electrodes.\textsuperscript{9}

![Figure 1.1 Scheme of Supercapacitor (EDLC)](image)

Electrodes and separator are immersed into electrolyte; ions in electrolyte can go
through separator and get close to the opposite charge. Double layers of charge will be
formed in each electrode due to the prevention for recombination of ions. Capacitance will
be generated from each double layers. Large surface area from carbon material and small
distance from double layers, these characteristics allow EDLC achieve larger capacitance
and energy density compare to traditional capacitors in same capacitor area.\textsuperscript{10}
Carbon material in EDLC will not have reaction during charge/discharge process, capacitance is only contributed by the double layer capacitance. For pseudocapacitor, the majority difference is chemical reaction happened during charge/discharge. The capacitance created by redox reaction called pseudocapacitance. Typically pseudocapacitance will be 10~100 times to the double layer capacitance with the same electrode area. Compare with EDLC, redox reaction will make the capacitor’s charge discharge speed decrease, but the additional pseudocapacitance can give larger specific capacitance and energy density than EDLC.\textsuperscript{11,12}

Two types of materials can be used as active material in pseudocapacitor, one is conducting polymers, and the other one is transition metal oxide. First pseudocapacitor was made by metal based material, metal based material has their advantage on cycling life, but the metal material is not environment friendly and the price is too high. Compare to metal oxide material, polymer based material is easy to fabricate and low cost. But the mechanical stress on polymers during redox reactions limited their cycling stability, the reduce of cycling stability will lead to a short lifetime for pseudocapacitors.\textsuperscript{13,14}
1.2 Electrochemical polymerization

For the polymer based electrode fabrication, electrochemical polymerization is one of the most efficient approach due to following advantages, first the monomer will directly deposited on the electrode surface, no further coating process required, it will provide good contact between substrate and material, also the films fabricated by electrochemical polymerization are more homogenous compared with drop cast; second, compared traditional poly-condensation reaction, electrochemical polymerization is catalyst-free reaction, the purity of polymer film will higher than traditional method.\textsuperscript{15-17} In addition, the deposition is controlled by the voltage and current put in the solution, which means this polymerization process can be precise controlled by external condition.

![Figure 1.2 CV curves for electrochemical polymerization](image)

Figure 1.2 CV curves for electrochemical polymerization
A typical electrochemical polymerization is showed in Fig 1.2, the internal curves is the first cycles, monomer’s oxidation peak can be observed in 0.7V, which means the polymerization will happen up the onset potential, material will be deposited in each cycle, from the figure the area of curve is gradually increase prove that the polymerization is happened. The advantage is the polymerization can be monitored by CV curves, the deposition amount can be controlled by the number of cycles, the disadvantage is polymerization only happen whether the voltage is higher than the oxidation potential, so the polymerization only happened in a small part of time.

A advanced method is used in this study, pulse method, a constant potential is put on the reactor and the monomers will keep polymerized, after some time, rest the reaction in order to make the monomer concentration and charged ions in solution back to homogenous, Then polymerized again, this polymerization-rest alternately method has higher efficiency than the CV method, with same reaction time, a thicker polymer film can be get with pulse method.

1.3 Bithiophene modified conjugated polymers

A novel phenanthridine based bithiophene modified conjugated monomer tert-butyl
3,8-di(2,2’-bithiophen]-5-yl)-6-oxophenanthridine-5(6H)-carboxylate was designed and polymerized as the active material on electrode, the molecular structure was showed in below, here we just simply called it PNBTH-Boc.
Previously a lot of research works were made in thiophene related monomer, however, the oxidation potential for single thiophene was around 1.6V, which is already an over oxidation potential for other material.\textsuperscript{17-19} Some strategy was demonstrated to decrease the monomer oxidation potential\textsuperscript{20}. Firstly, multi thiophene functional group like bithiophene unit has relatively low oxidation potential, Secondly, introduce some conjugated structure into molecular, large conjugated structure can help to reduce oxidation potential due to the increase of charge capacity.
1.4 Overall Material Synthesis route

![Synthesis route for PNBTH polymer](image)

**Figure 1.4 Synthesis route for PNBTH polymer**

**Reaction Condition**

1. 98% H2SO4, NaN3, 2h, 0°C, N2 protection

2. THF, DMAP, di-tert-butyl dicarbonate, 3h, rt, N2 protection

3. THF, Pd(PPh3)4, bithiophene, 0°C, 10h, N2 protection

4. 1mg/mL PNBTH solution in DCM, 0.1M TBAPF6 solution in PC, 100cycle polymerization, rt, Argon protection

5. 220°C, 10min, Argon protection
CHAPTER II

EXPERIMENT SECTION

2.1 Materials

Sulfuric Acid, 98%, Fisher Chemical

THF, 99.7%, Fisher Chemical

Methanol, 99.7%, Fisher Chemical

Hexane, 99.7%, Fisher Chemical

Dichloromethane, 99.7%, Fisher Chemical

Sodium azide, 99.9%, Sigma-Aldrich

Tetrabutylammonium hexafluorophosphate, 99%, Sigma-Aldrich

Pyr14TFSI Ionic liquid, 97%, Ionic liquid technology

Propylene carbonate, 99.7%, Sigma-Aldrich

2,7-dibromofluorenone, 98%, Alfa Aesar

4-Dimethylanilinopyridine, 3.0mmol/g, Sigma-Aldrich

di-tert-butyl dicarbonate, 97%, Alfa Aesar

Tetrakis(triphenylphosphine)palladium(0), 99%, Alfa Aesar
Sodium Chloride, 99%, Alfa Aesar

Sodium bicarbonate, 99.5%, Alfa Aesar

2.2 Instrumentation and Instrumental techniques

TGA:

Electrochemical Analyzer: CHI 608E

CVD system

Electron Beam Evaporator

2.3 Monomer Material Synthesis

The synthesis route for monomer PNBTH-Boc was following pervious literature\textsuperscript{21}.

The synthesis detail is showed below.

\[
\begin{align*}
\text{1} & \quad \text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{O} & \quad \text{Br} \\
\text{O} & \quad \text{NH} \\
\text{3,8-dibromophenanthridin-6(5H)-one (PN)}
\end{align*}
\]

8.1g 2,7-dibromofluorenone (1, 24mmol) was added into 150mL flask and dissolved in 60mL 98% sulfuric acid under room temperature, 3.68g NaN\textsubscript{3} was added into solution in half hour with N2 protection. The mixture was stirred for two hour then poured into ice
and keep stirring. The precipitation in solution was collected by filtration and washed by water and hexane, 7.70g product PN was collected after dried in vacuum. $^1$H NMR (300 MHz, DMSO-d6) δ8.46 (d, 1H), 8.35 (q, 2H), 8.01 (q, 1H), 7.53 (d, 1H), 7.42 (q, 1H), 11.88 (s, 1H, N-H hydrogen bond).

Tert-butyl 3,8-dibromo-6-oxophenanthridine-5(6H)-carboxylate (PN-Boc)

Under N$_2$ protection, 4.23g PN (12mmol) and 1.46g DMAP were added into 150mL flask and dissolved in 70mL anhydrous THF, 5.57g di-tert-butyl dicarbonate (30 mmol) was slowly added into solution, the mixture was stirred around 3 hour and checked with TLC, after reaction the majority solvent was removed by rotate evaporator and remained part was poured into 40mL 5% NaHCO$_3$ solution. The precipitation were filtered and washed by water, then dissolved in DCM and dried with Na$_2$SO$_4$, rotate evaporate again and precipitated in 20mL MeOH, 3.80g pale yellow product (71%) was collected after precipitation. $^1$H NMR (300 MHz, CDCl3) δ8.60 (d, 1H), 8.05 (q, 2H), 7.89(q, 1H), 7.46 (q, 1H), 7.30 (d, 1H), 1.72 (s, 9 H).
0.5g PN-Boc and 64mg Pd(PPh$_3$)$_4$ were added into 100mL flask under N$_2$ protection, 20mL anhydrous THF was added into flask, 2.02g trimethyl tin bithiophene was dissolved in 5mL anhydrous THF and slowly dropped into flask, the mixture was heated to reflux for 3h, after cooled down, 50mL DCM was used to diluted the mixture, the solution was washed by water and brine for two times, then the washed organic phase was dried by Na$_2$SO$_4$, solvent was removed by rotate evaporator, then the solid was dissolved again by small amount of DCM, precipitated in Hexane. 0.515g (74.6% yield) orange product was collected after precipitation.

2.4 Polymer electrode fabrication and characterization

All electrochemical experiment data was carried out using a CHI 608E electrochemical analyzer inside a glove box with argon atmosphere. Monomers were electrochemical polymerized and deposited on ITO glass by Chronoamperometry method (Potentialstatic Deposition Scans) in a three electrode device, platinum wires were used as counter and reference electrode and ITO glass was used as working electrode. 1mg/mL monomer in dichloromethane solution was mixed with 0.1M TBAPF6/PC supporting electrolyte in 3:1 volume ratio. Electrochemical deposition was controlled by the length of pulse and
numbers of cycles. The optimized condition for polymerization was 100 cycles with 30s 0.9V pulse and 30s 0V pulse. After polymerization, the coated ITO electrode was putted on a hot plate and annealed under 220°C for 10min to remove the Boc group in polymer. After annealing process, by the same three electrode device containing 1:1 ratio of PYR14TFSI/PC electrolyte, the immobilized polymer electrode was activated under 1.6V chemical window, 10mV/s scan rate for 10 cycles.

2.5 Carbon nanotube electrode fabrication

Carbon nanotube was grow on stainless steel substrate by super growth method. One piece of stainless steel foil was deposited with 10nm Al2O3 and 1.5nm Fe by E beam evaporator, the catalyst coated substrate was cut into bar shape and put into sample tube and load into CVD tube funnel, the CVD system was first heated to 750°C and purge with Argon and hydrogen, under hydrogen atmosphere, the sample was annealed under 50ppm/s H2O/H2 for 3min, after 3 min annealing 100ppm/s C2H2 was added into system as carbon source, CNT was grown under this condition for 10min, after growing the sample was transfer out of the heating zone and cooled under hydrogen flow.

2.6 Supercapacitor Device fabrication

The device was fabricated by one piece of polymer ITO electrode and one piece of CNT electrode. Polymer electrode was used directly after activation. Both electrodes were
scratched to 0.5cm X 0.5cm. One piece of Celgard 2500 was used as separator. All these parts were wet by PC:IL=1:1 electrolyte before fabrication, the supercapacitor device was fabricated follow fig 2.1, a clamp covered with kepton was used to hold this device. Polymer electrode was connected with working electrode, CNT electrode was connected with counter and reference electrode.

Figure 2.1 Scheme and photo of supercapacitor device fabrication.

2.7 Flexible Aluminum substrate electrode fabrication

The aluminum foil was cut and folded into rectangle shape, the top of electrode was folded to smaller rectangle in order to fit the reactor. Each board was folded again to sealed the inside. The shape was showed in figure below, the folded substrate was deposited with 1.5nm titanium and 40nm gold by E-beam evaporator. After deposition, the coated electrode was clamped into reactor, follow the same procedure to electrochemical polymerization which was used in ITO substrate.
Figure 2.2 photo of flexible electrode
CHAPTER III

RESULT AND DISCUSSION

In this chapter, all the single electrode electrochemistry performance was measured by electrochemical analyzer under 3-electrode cyclic voltammetry method and charge/discharge method. The device was measured under 2-electrode setup. All experiments were done inside the glovebox.

3.1 Electrochemical polymerization and activation condition

The reactor was modified by a 4mL vial, two platinum wires served as counter and reference electrode, a stainless steel clamp was used to hold ITO or other electrode substrate and used as working electrode. Instrument was showed in Fig 3.1, during the experiment, changing from monomer solution to ionic electrolyte can be finished by changing vials, furthermore, enclosed environment can prevent electrolyte evaporation, which will lead to a reduced coated area.
3.2 Electrochemical polymerization and activation

The monomer’s oxidation onset potential was influenced by the solution conductivity, it was difficult to make solution with totally same concentration each time, so the polymerization potential need to be measured first. Before polymerization, one cycle of cyclic voltammetry was run to determine the location of monomer’s oxidation peak. Fig 3.2 showed the cyclic voltammetry curves, from the figure the oxidation peak was located around 0.9V, so the polymerization potential was set to 0.9V. Fig 3.3 showed 100 cycles potential static deposition, the end points of oxidative curve become higher and higher, which means more material is deposited on the electrode and the polymer film become more conductive.
Figure 3.2 monomer oxidation potential measurement

Figure 3.3 100cycles Polymerization under pulse method
Table 1 shows the comparison of area capacitance from different polymerization conditions. 30s pulse with 100 cycles can get largest area capacitance. From this table, experiment one and two determined that more material deposited on the electrode will provide more capacitance after activation, however, 60s pulse cannot get capacitance enhanced after activation, during the polymerization, 60s pulse can polymerized longer chains compared with 30s, long chain will suffer with higher mechanical stress during activation and possibility break or decomposed under high voltage.

<table>
<thead>
<tr>
<th>condition</th>
<th>50x30s</th>
<th>100x30s</th>
<th>50x60s</th>
<th>100x60s</th>
</tr>
</thead>
<tbody>
<tr>
<td>capacitance</td>
<td>42.7mF/cm²</td>
<td>95.0mF/cm²</td>
<td>break</td>
<td>break</td>
</tr>
</tbody>
</table>

Boc group will be removed around 180°C based on the TGA spectrum for PNBTH-Boc. After polymerization, electrodes were annealed under 200°C for 20min on hot plate in order to fully remove Boc group from the polymer film, which can make the polymer become totally insoluble, furthermore, Boc group will be decomposed to CO₂, which can generate a lot of hole structures on the polymer film surface, Fig 3.5 showed the SEM images before and after annealing, after annealing the film surface become porous, this morphology change can enlarge the surface area of electrode, the capacitance will increase due to more material can contact with electrolyte during the electrochemical measurement. After activation the hole structure become not so clearly, due to the high boiling point
solvent used in activation, possibility explanation was hole was filled with electrolyte, which made it not so clearly in the SEM image.

Figure 3.4 TGA spectrum for PNBTH-Boc
Figure 3.5 SEM images for PNBTH polymer film, A) and a): before annealing. B) and b): after annealing C) and c): after activation
The annealed film were clamped by the same device with PC/IL electrolyte. Initially there was almost no capacitance under the potential which used in the polymerization, the area capacitance was less than 1mF/cm\(^2\). However, an activation process would happen if a higher potential was putted on the electrode, fig 3.6 A) showed CV spectrum for activation, on the first cycle there was no peaks in the range of 0.4V to 1.4V, after first cycle, two peaks can be observed around 1.2V and 1.5V, and peaks height were gradually increased during cycling, after 10 cycle’s activation the capacitance can reach the maximum around 100mF/cm\(^2\). Possibility explanation for the phenomenon is cross-linking happened due to the color change, fig 3.6 B) shows the change is permanent because the color will never back to original, also reaction can still happen if the electrode is cycled in a smaller chemical windows after cross-linking.

Figure 3.6 A) CV spectrum for activation process on PNBTH electrode. B) Image for electrode color change before (left) and after activation (right)
3.3 Properties of Activated Electrode

The CV for activated electrode in the three electrode device at scan rate ranging from 5mV/s to 500mV/s and the result are shown in Fig 3.7, with the scan rate increase the areal capacitance will gradually decreased because the polymer film need time to response the potential change, reflect in the figure, the oxidation onset point will shift to higher voltage with scan rate increase, as a result, under same chemical window, the range of oxidation will decrease due to the oxidation peak shift, less material involved in redox reaction and lower the capacitance. Also, from fig 3.8, with charge/discharge in different current density, the voltage drop will become larger stand for the increasing of internal resistance.

Figure 3.7 CV spectrum for PNBTH electrode under different scan rates
The cycling stability test was carried out from cyclic voltammetry method, 100mv/s scan rate and two different chemical window 1.2V and 1.5V were used as cycling conditions. However, the result was not as good as expected, the electrode can only keep 50% initial capacitance after 1000 cycles under 1.5V chemical windows, the majority degradation happen in the second oxidation peak, if a smaller chemical window like 1.2V applied, the cycling performance increased to 80% capacitance remaining after 1000 cycles, but even that it still means not so stable during cycling.

Figure 3.8 Charge/Discharge spectrum for PNBTH electrode under different current density
Figure 3.9 Capacitance for cycling stability test under different chemical windows

To find the problem during cycling test, the used electrode was taken the SEM image after washed. SEM images showed there were a lot of cracks on the polymer film and part of material was peeled off from the electrode, which means the majority reason for capacitance decrease is material lost, possible reasons for polymer peeled off could be degradation or poor adhesion between polymer and ITO, first reason means the material itself was unstable and polymer chain will break down during cycling, second reason means material was stable, but the bad adhesion made material was too easy to separate with ITO glass, although conjugated polymer was conductive, the conductivity of polymer was no comparable with ITO, the electrons will prefer directly go through the ITO, so the peeled off material will no longer have their function.
Figure 3.10 A) SEM for image for polymer electrode after cycling test B) Photo of polymer electrode after cycling test

The impedance factor were measured after polymerization, after annealing and after activation, the spectrums were showed in fig 3.11, the initial fitting $R_{ct}$ was 108 $\Omega$ after polymerization, the $R_{ct}$ was decreased to 61 $\Omega$ after annealing and decreased to few ohm after activation, possibility because the molecular packing changed after the boc group leaving and crosslinking, smaller $R_{ct}$ means polymer become more conductive, also after activation, the expansion of conjugated structure will provide higher conductivity and lower the polymer’s resistance.
Figure 3.11 Impedance spectrum for PNBTH electrode
3.4 Supercapacitor device characterization

The assembled device was first measured with different chemical window in CV method and showed in fig 3.12, a sharp peak appeared after 2.8V, which probably came from the degradation of material or electrolyte. In order to get better device stability in cycling test, a safety chemical window 2.8V was used in all device electrochemical measurement.

![Graph showing CV for supercapacitor device under different chemical window](image)

**Figure 3.12 CV for supercapacitor device under different chemical window**

To evaluate the electrochemical performance of supercapacitor, the device was tested with CV and charge/discharge measurement, the CV and charge/discharge spectrum were different from those in single electrode measurement, because the CNT electrode will also
provide double layer capacitance, the capacitance contribution from CNT made the polymer peaks not so clearly from the spectrum, but the curve’s slope change still indicate that there was pseudocapacitance generated from the device.

Figure 3.13 CV under different scan rate.

The capacitance were calculated by charge/discharge data and showed in table 2. The charge/discharge result showed the device can be run in higher current density, compared with single electrode measurement data, the device can be scanned with 10mA/cm², and the single polymer electrode can only be scanned with maximum 1mA/cm², which means the device can get large power density. The capacitance will also decrease when the current density increase due to the pseudocapacitance, but the decrease rate was not as large as
those in single electrode. Because the CNT itself will provide some double layer capacitance. Also the CNT can help to stable the device.

Table 2 Electrochemical performances under different current density

<table>
<thead>
<tr>
<th>Current density</th>
<th>10mA/cm²</th>
<th>5mA/cm²</th>
<th>2mA/cm²</th>
<th>1mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area capacitance</td>
<td>16.45mF/cm²</td>
<td>18.57mF/cm²</td>
<td>21.14mF/cm²</td>
<td>21.57mF/cm²</td>
</tr>
<tr>
<td>Energy density</td>
<td>232.2μWh/cm²</td>
<td>262.1μWh/cm²</td>
<td>298.4μWh/cm²</td>
<td>304.4μWh/cm²</td>
</tr>
<tr>
<td>Power density</td>
<td>28.0mW/cm²</td>
<td>14.0mW/cm²</td>
<td>5.6mW/cm²</td>
<td>2.8mW/cm²</td>
</tr>
</tbody>
</table>

Figure 3.14 Charge/Discharge under different current density.
There was only limited space so the material peeled off problem would not be so critical if there was not too much degradation happen. The device cycling stability test was measured by charge/discharge method within the chemical window 2.8V at a current density 10mA/cm$^2$ and the result was showed in fig 3.15, not like the single electrode result, the device could remained 85% initial capacitance after 10000 cycles, fig 3.16 showed the charge/discharge curves before and after cycling test, from the figure there was almost no shape changes from the discharge curve, this result proved that most of polymer material was stable during cycling.

The excellent cycling performance on a pure polymer electrode can be explained by following reasons. First the stable voltage was put on the device made the material avoid over charge and discharge and prevent degradation. Second the cross-linking during activation had created a large conjugated structure which can stand for mechanism stress from molecular expansion and shrinkage. Also the excellent cycling result provide evidence that bad cycling result from single electrode cycling test was majority caused by bad adhesion between polymer and ITO. Polymer itself was stable during cycling.
Figure 3.15 cycling stability test under charge/Discharge method for 10000 cycles.

Figure 3.16 Charge/Discharge before and after 10000 cycles
3.5 Flexible aluminum electrode fabrication

One of the advantage for ITO glass was single face conductive, material will only deposited on one side, however, it will also became a disadvantage in device fabrication, because glass cannot be conductive in vertical direction, so we cannot use something like coined cell to fabricated closed device. Metal sheet or foil used as substrate which is conductive in vertical direction will face another problem, the material will be deposited everywhere conductive, and the back side will also coated material. Thus, a method to protect the back side need to be carried out for this experiment.

Here we demonstrate a simple way to meet this requirement, just folded the aluminum foil, the back side will be protected by foil itself. The seam in the border can also be sealed by folding. After deposition, the back part can be directly removed by cutting, because there was no solution contact with the back side of aluminum, finally a one side coated electrode can be get.

At the first attempt, Aluminum foil only electrode was used as substrate, however, some oxide thing on the top of electrode made the deposition not homogenous, so additional conductive layer was required for this deposition.
40nm gold was deposited first by E-beam evaporator to optimize the electrode surface conductivity, however, after several cycles polymerization, gold layer was peeled off from the aluminum, which means the adhesion between gold and aluminum was not strong. Too reinforce the adhesion between gold and aluminum. Additional adhesion layer like titanium or aluminum oxide was required, because we need to get enough conductive in vertical direction, in this case, 1.5nm titanium was used as adhesion layer.

The polymerization on Au-Ti-Al substrate worked well, after 100 cycles a thick polymer film can be acquired, thickness larger those can be got from gold substrate because gold has low resistance compared with ITO glass. After polymerization, the electrode was
gone through the same annealing and activation process, same color change can be observed during activation. After disassemble, the back side is clean and no deposition,

Figure 3.18 polymer deposited on Al-Ti-Au substrate

Two pieces of polymer electrodes was used to fabricated symmetric supercapacitor device, however, CV curve was totally different from the asymmetric one, the redox peaks were separate in two sides and the area capacitance was less than 5mF/cm² in 10mv/s scan rate, also the stability of device was not as good as the pervious discussed asymmetric ones, the peaks will keep shifting during cycling, the device can only suffered with 500 cycles and the capacitance will decrease to 20%.
after disassemble, we found even with adhesion layer, the gold layer will still peeled off from the aluminum, the increase of contact resistance caused the peak shifting, which made the oxidation happened out of the chemical window, and finally lead to the capacitance decrease.

These result showed the aluminum was not capable for the flexible electrode substrate, but the back side protect design was succeed, so in the future we only need to find some property substrate with better adhesion with gold and replace the aluminum, the rest condition can be kept.
A novel multi-thiophene conjugated polymers were synthesized via electrochemical polymerization. After a unique activation process, the single electrode capacitance can be enhanced more than hundred times and stable in this activated stage. The highest single electrode capacitance achieved, 112.5mF/cm$^2$ under 1mA/cm$^2$ current density after activation. The asymmetric supercapacitor fabricated by PNBTH polymer electrode and CNT electrode can be cycled 10000 times and still kept 85% initial capacitance. 304.4μWh/cm$^2$ energy density can be achieved at a power density of 2.8mW/cm$^2$ and retained 232.2μWh/cm$^2$ at even ten times large power density 28.0mW/cm$^2$. Such good cycling performance was carried out from a pure polymer electrode, showed this type of “polymerization-activation” system has potential to produce variety of stable conjugated polymer electrodes. In addition, the electrode was fabricated by electrochemical polymerization, as a solution process, which means it is easy to fabricated electrodes with large area or specific shape.
In the future, property substrate with better adhesion with gold will be found and used for flexible electrodes experiment, also the in-plane structure supercapacitor device can be tried because electrochemical polymerization can easily deposit in designed shape like hair-brushed, which is widely used in in-plane supercapacitor.
BIBLIOGRAPHY


