High-volumetric-energy-density redox-active polymer batteries

Minsun Kang

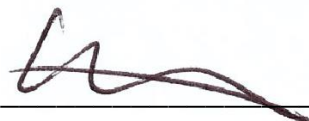Department of Energy Engineering

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High-volumetric-energy-density redox-active polymer batteries

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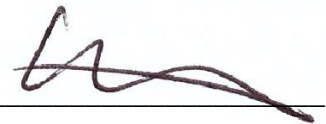
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Major Advisor

Hyun-Kon Song

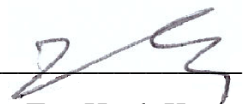# High-volumetric-energy-density redox-active polymer batteries

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Abstract

Lithium ion batteries (LIBs) have conquered the energy storage device market due to its high energy densities. Even higher densities are being pursued as LIBs' applications are extended from small devices to larger ones including electric vehicles and energy storage devices. Energy densities (EDs) can be considered from two different bases: mass and volume. Volumetric EDs should be emphasized in space-limited situations even if gravimetric EDs are more considered in literatures. Here we demonstrate lithium metal | redox-active polymer batteries showing high volumetric EDs. Polyvinylcarbazole (PVK) was used as an organic redox-active material while polyvinylidene fluoride (PVdF) and carbon black were used as a binder and a conducting agent respectively. The high volumetric EDs were achieved by spray deposition that we emphasize as a novel electrode-fabrication process in this work. The mixtures of the electrode components in solvents were spray-deposited on current collectors. Tiny droplets (size = 50um) containing the components were generated from nozzles. Solvent of the droplets were rapidly evaporated during the time of flight as well as when they met heated current collectors. The components originally included in the droplets were densely packed on the current collectors. The electrode densities achieved by the spray deposition were several times higher those of conventional blading methods. Accordingly, several times higher EDs were obtained from our lithium metal | redox-active polymer cells when compared with the cells prepared by blading methods. The volumetric ED gains overwhelmed the loss of porosity leading to mass transfer problems so that the volumetric EDs of spray-deposited electrodes were higher even at high rates than those of bladed electrodes. We expect that the spray deposition method is appropriate for preparing all-polymer-flexible batteries while conventional inorganic materials can be deposited by the method.

Contents

1. Introduction

1.1 Lithium ion batteries

Fossil fuels bring environmental problems such as emission of CO_2 which contribute to global warming in earth. Hydrologic cycle changing, global climate problems come out an issues. Also shortage of fossil fuel deposits causes fluctuation of price.[1-2] To solve these problems, environmental-friendly energy technologies are required. Green energy like solar and wind velocity will be main energy of industry and living before long that is unlimited resources and eco-friendly.[3-4]

Green energy sources could be stored in batteries as chemical energy which converse to electrical energy when using electric devices **(Figure 1.1)**. Among batteries, Li-ion batteries (LIBs) are outstanding in energy density of 150Whkg^{-1} so lots of energy could be stored. Li-ion batteries are composed main four materials like cathode, anode, separator and electrolytes. Cathode materials includes lithium cobalt oxide (LCO), lithium manganese oxide (LMO) and Lithium iron phosphate (LFP) while the most representative and widely used anode material is graphite.[5-6]
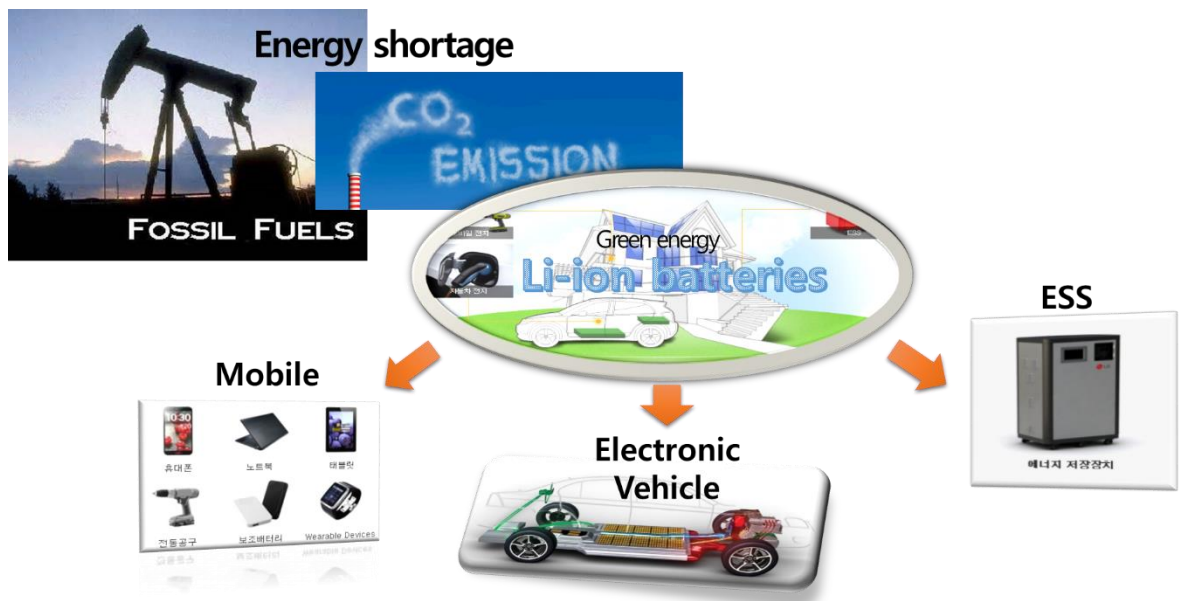

Figure1.1. Energy problems by using fossil fuels and the utilization of Li-ion batteries.

There is principle of LIBs. When charging state, Lithium ions come out from the LCO and go to graphite through electrolyte and separator. In electric wire, electrons also move to anode parts. Lithium ion intercalated in layered structure of graphite. Due to adequate space between layers, lithium ion could remained stable in graphite. The potential gap between cathode and anode become large and then energy could be stored in batteries at open circuit state. When connecting the application, electrons flow through electric wires in application.[7-8]

Li-ion batteries (LIBs) are divided in terms of its size. Small size used to mobile application such as cellphone, notebook and tablets. Medium are used to electric vehicle. Large size are using to energy storage system (ESS). Due to their suitable performances, Li-ion batteries have been commercialized at portable devices long before and aggressively dominated market filed of electric vehicles (EV) and energy storage system (ESS).

EV is attracting as green cars in global market and the scale will be 20 percent increase annually. ESS market also will be fast growing as advanced country have a lot of interest and developed for the third industrial revolution. The requirement that Li-ion batteries completely settle down is low cost, safety, abundant component and prolonged cycle life. Also energy density should be developed more and more.

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1.2 Organic electrode batteries background

Inorganic electroactive materials such as lithium transition metal oxides have been widely used as cathode materials for LIBs. Many efforts have been devoted to increasing their capacities and stabilizing their structures during repeated charging/discharging operations for guaranteeing longer discharging time and more operation frequencies of LIBs.[9-10] Transition metal such as cobalt in the inorganic cathode materials causes concerns about their limited resources and environmental pollution issues.

On the other hand, organic materials have flexibility which is come from intrinsic elastic property of polymer and low cost effect. We could obtain certain characteristic by synthesizing various functional groups.[11] Numerous experiments have been tried to apply redox-active organic materials to electrode active materials in batteries for several decades.[12-13] Redox-active organic materials have been developed since dichloroisocyanuric acid (DCA) as a N-chloro compound was reported in 1969. Conducting polymers and organic sulfides were comprehensively studied in 1980s to 1990s. Nitroxyl radical polymers and conjugated carbonyl compounds have been ongoing popularly nowadays.[14] In aspect of electrochemical performances organic material electrodes have high density, power density and cycling stability. However it is still early stages for commercialized batteries.[15]
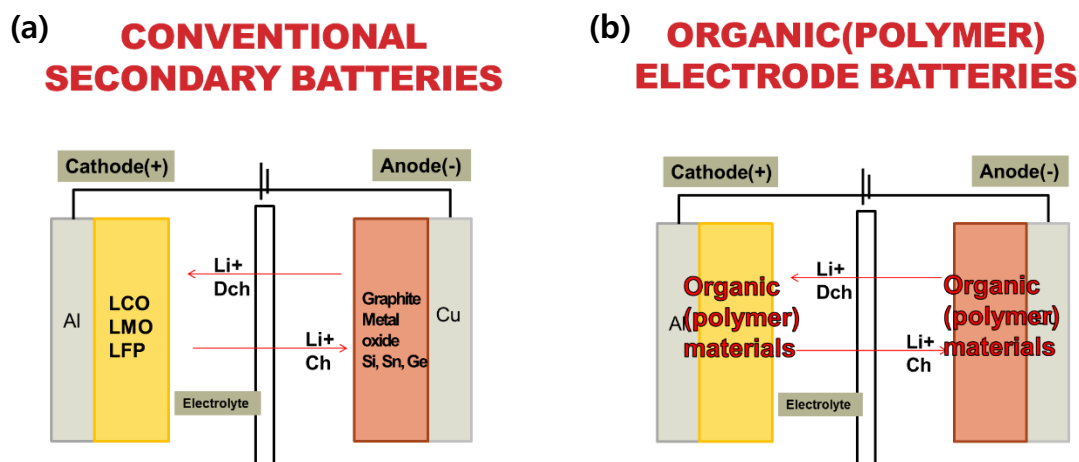

Figure 1.2. The comparison of (a) conventional secondary batteries and (b) organic electrode batteries.

A LIB cell is composed of two electrodes (a cathode and an anode) with electrolyte and separator **(Figure 1.2a)**. The redox-active materials of different reduction potentials were used for

developing electromotive forces after charging. The cells are charged by oxidizing the material of more positive reduction potential and reducing the material of more negative reduction potential. The oxidized and reduced materials during charging process are called cathode and anode, respectively. According to the basics of electrochemistry, the naming is not exactly correct because the electrodes on which oxidation proceeds should be called anodes. However, cathodes and anodes are defined when the cells are discharged in cases of energy storage devices. While the electrochemical reactions proceed, lithium ions are released from the cathodes because lithium ions are not attracted any more by transition metals that are oxidized. At the same time, reduced anode materials experience deficiency of lithium ions so that lithium ions are incorporated to the anode materials. Therefore, electrochemical reactions in LIBs involve lithium-ion-relevant faradaic reactions in addition to charge neutralization of the ions as the non-faradaic process.

As the organic counterparts of the conventional inorganic materials for cathodes, Redox-active organic materials can be also used as active materials in the same configuration only if they have reduction potentials different from those of the other electrode **(Figure 1.2b)**. They can replace inorganic cathode materials, anode materials and both of them. The property of organic redox-active materials most distinguished from its inorganic counterparts is that they are based on redox-activities that are not relevant to lithium ions. In other words, the lithium ions can be replaced by other cations, playing a role of charge neutralization. Only nonfaradaic (NOT faradaic) processes are involved from the viewpoint of lithium ions while electroactive sites of the organic materials are surface-confined on electrodes. Therefore, there is every possibility that charge transfer kinetics of the organic are more facile than that of the inorganic.[16] In addition to the fast kinetics leading to high power in electrochemical cells, merits of organic compounds and polymers as electroactive materials for energy storage devices could have structure diversity, flexibility and sustainability.

The redox-active organic materials are classified into three types according to the faradaic reactions of their as-received states **(Figure 1.3)**. N-type materials are reduced while P-type ones are oxidized. Bipolar materials can be both reduced and oxidized. Incorporation or influx of cations (Li^+, Na^+, K^+ and H^+) and anions (ClO_4^-, PF_6^-, BF_4^-, $TFSI^-$) to electrodes are required for keeping neutrality in N-type and P-type materials, respectively. When batteries are constructed based on organic materials for both electrodes, N-type and P-type materials should be paired.[17]

The demerit points that are exist on redox-active organic materials. The organic polymer are dissolved in electrolyte of batteries that is fatal blow as electrode active materials. Moreover low electronic conductivity of polymer interrupts efficient flow of electrons and ions in circuit of battery

system. Although enormous research have been investigated on various organic materials, it is hard work to get over these problems perfectly. In the future, we need to reduce candidates for organic electrode materials and focus on possibility about commercialization of organic electrode redox-active materials.
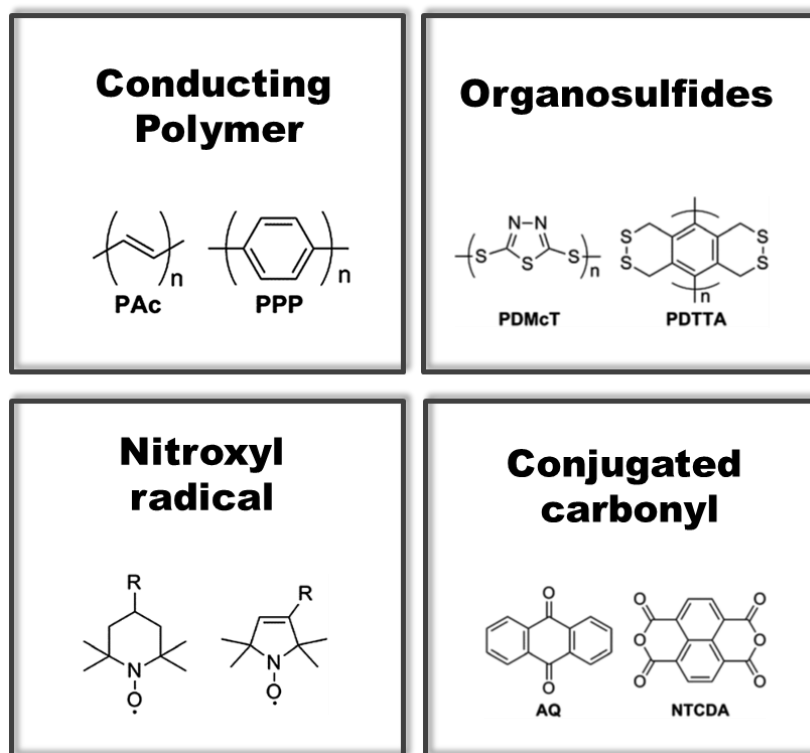

Figure 1.4. The main four type of organic electrode materials.

In several decades, a lot of organic electrode materials have been investigated. And there are main four types in structures and redox reaction mechanisms (**Figure 1.4**).[18] First is conducting polymers that have electric conductivity in conjugated polymer structures. Second, organosulfides have sulfur single bond in materials which have high theoretical capacity by sulfur atom. Third, nitroxyl radical has reactive free radical with high reaction. Finally, conjugated carbonyl compounds. It has carbonyl group. Conducting polymer and organosulfide compounds have been investigated from 1980 to 2000 and nitroxyl radical and conjugated carbonyl compound have been extensively studied from 2000 (**Figure 1.5**).

Structure		Redox mechanism	Examples
Conducting Polymer (1981-)	Conjugated hydrocarbon		PAc, PPP
	Conjugated amine		PAn, PPy
	Conjugated thioether		PTh, TA
Organosulfur Compounds (1981-)	Organodisulfide (1981-)		PDMcT, PDTTA
	Thioether(4e) (2007-2009)		PEDOT, PTBDT
Nitroxyl radical (2002-)			
Conjugated carbonyl (1969-)			AQ, NTCDA

Figure 1.5. The history of organic electrodes.[17]

1.2.1 Sulfur compounds

Bond-cleavage/formation mechanism

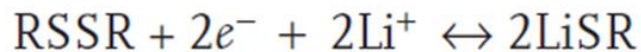$$RSSR + 2e^- + 2Li^+ \leftrightarrow 2LiSR$$
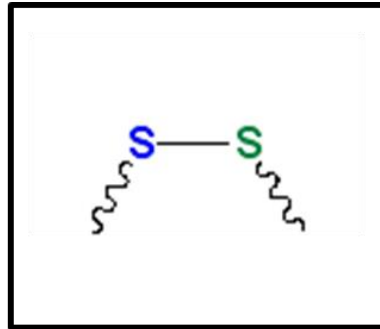
Figure 1.6. The molecular structure of sulfur compounds and mechanism of it.

Organosulfur compound is composed of S-S bond. The mechanism of redox reaction is **Figure 1.6.** Di-sulfur bond get two electrons that is reduction state. The bond is broken into two sulfur then thiolate anion occurs. Lithium ions close to this thiolate anion to compensate charged states. A reverse way would be same. When losing two electrons, it is oxidation state. Sulfur atoms are combined together and Lithium ions are get out from the sulfur bond. This is the bond-cleavage/formation mechanism which could get two electrons in redox reaction.[14, 19]
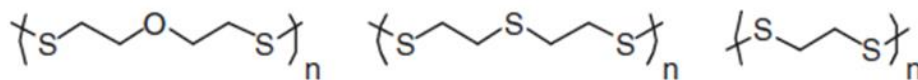
Figure 1.7. The structures of main chain type organosulfur polymers.[13]

There are several types in organosulfur compounds. First, it is main-chain type organosulfur polymers **(Figure 1.7)**. This is first class of organosulfur cathodes that have disulfide bonds in the main chain. It is capable of delivering high energy density because sulfur atom has high capacity compounds.[20] The most popular materials is 2,5-dimercapto-1,3,4,-thiadiazole (DMcT). However it has low redox reaction rate which need operating at high temperature. DMcT also is not electrically

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conducting then electro-catalyst was added to accelerate the sulfur bond-cleavage/formation mechanism.[21-24]

Reversible Electron Transfer Reaction
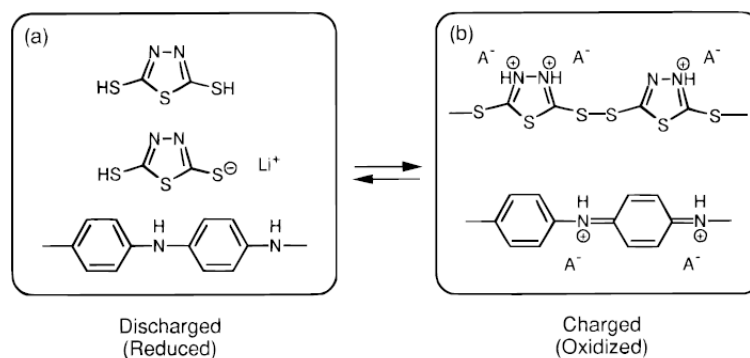
Figure 1.8. Schematic diagrams for discharged and charged state of DMcT-Pan.[25]

As electro-catalyst, polyaniline which is conducting polymer was used. When joining DMcT and polyaniline, reversible electron transfer reaction could be possible (**Figure 1.8**). Polyaniline oxidized DMcT in charged state and reduced DMcT in discharged state that means two materials exchanged the electrons resulting in high redox reaction rate. Then the capacity of this cell was 186mAh/g satisfying 80% of theoretical capacity.[25] As electro-catalyst, PEDOT conducting polymer was used in another paper which resulted more electro active reactions.[26-27]
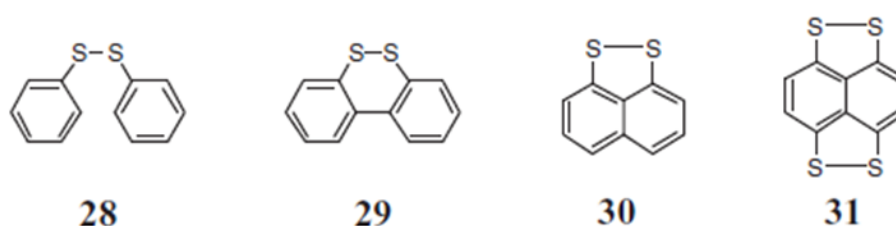
Figure 1.9. The structures of side chain type organosulfur polymers.[13]

However, main chain type organosulfur polymer such as DMcT was dissolved in electrolytes. Thiolate anion was soluble in common electrolyte making capacity fading.[28-30] Second type occurred that was side-chain type organosulfur polymers **(Figure 1.9)**. This is second generation of organosulfur electrode. Disulfide bonds is located at the side chain. When redox reaction occurs, main chain is not broken. It leads to capacity retention and recombination efficiency.[31] Different type of polyamide was compared that was cyclic polyamide (DTA) as side chain type and linear polyamide (GTA) as main chain type. As a result, DTA or side chain type organosulfur compounds showed higher capacity retention that GTA or main chain type (Figure 1.10). Because side chain types was not divided into electrolytes.[26]

Figure 1.10. The energy density of DTA and GTA polymers.[26]

1.2.2. Conducting polymers

Conducting polymer has been used for batteries and capacitors.[32-34] Common polymers do not have conductivity. However electron could move along polymer backbone in conducting polymers. Three mans got nobel prizes in 2000 for discovering and studying these conducting polymers. One of them, Shirakawa synthesized a polyacetylene and the others, Heeger and MacDiarmid put iodine halogen into polyacet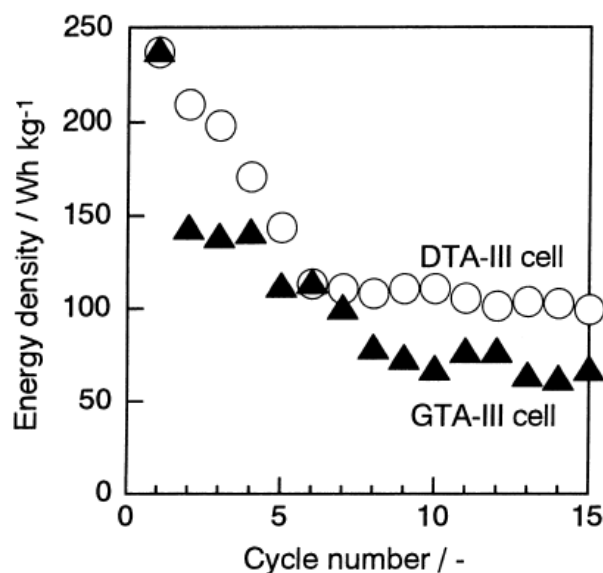ylene **(Figure 1.11)**.Then polyacetylene as insulator became conductive.[35-42] **Figure 1.13** shows conductivity of the materials which is divided into three parts as insulator, semiconductor and metal. The conductive rage of conducting polymers is from insulator to metal.

Figure 1.11 Three man who got novel prize for conducting polymers.

Electric conductivity means that electrons could move out of atom which is determined by electronic structure. In atomic model, there is one nucleus and electrons move around it. Electrons exist in several electron shells with each specific energy level. When two atoms meet, energy levels in one atom and another atom overlap together then bonding of three atoms is also possible. If a large number of atoms meet, the size of energy level is broad which causes continuous energy level. It called energy band. In conducting polymer like polyacetylene, carbon atoms and hydrogen atoms meet and make continuous energy band. This band consists of three parts that is valance band, conduction band and band gap. Valance band is filled with electrons with low energy while conduction band is empty. Band gap means energy gap between valance and conduction band. The electrons in valance band could not move since it is full. If electrons in valance band get energy, it could jump to the conduction band where electrons move easily. To reach for conduction band,

electrons have energy surpassing the band gap. Actually, original conducting polymer have big band gap so it is hard to make electrons jump compared to metal and semiconductor.
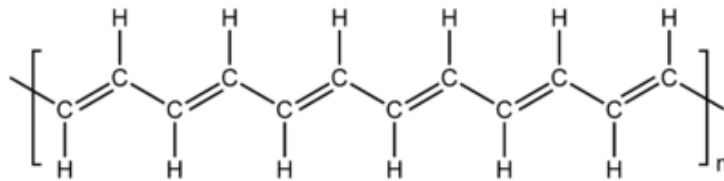

Figure 1.12 Structure of polyacetylene polymer.

The structure of conducting polymer is conjugated which is alternating a single bond and double bond **(Figure 1.12)**. Bonds in benzene molecule are mixed and become equal with all same length which called resonance. Bonds in conducting polymer are not resonance and it is localized. And Conducting polymers have amorphous morphology so electrons have to jump from one chain to next chain. So there is not conductive itself.

The answer of making conductivity in polymer is doping which means putting impurities to materials. Oxidation and reduction reaction occurs from doping. When putting iodine molecule into the polyacetylene, iodine molecule attracts electrons from polymer chain and get electrons. Then polymer chain become positive charged state that is conductive. To explain doing for classic band gap theory is not possible. Instead of band gap theory, polaron band model appears. Radical is one unpaired electron. After oxidation, radical cation is obtained in polymer that polaron. The unpaired electron moves easily along double bond in conducting polymer while positive charge is fixed. There is electrostatic attraction bewtween iodidie ion and positive charge so that iodide ion makes electron stop. To help positive charge move, a high concentration of counter ions is required. Putting more iodide ion is attracting positive charge then polaron cloud move to close counter ions. When explaining polaron as band gap, band gap need to be modified. After oxidation, polymer forms a polaron which making certain band in the middle of band gap. This called polaron band. Energy level gap among valance, polaron and conduction band becomes small than first. Electrons move easily through jumping bands.

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Name	Structure	Doping level (x_{max})	Theoretical capacity/ mA h g^{-1}	Redox potential (V vs. Li^{+}/Li)
Polyacetylene (PAc)		0.07	144	0–2.0 (n) 3.5–4.0 (p)
Polyparaphenylene (PPP)		0.4	141	0–1.0 (n) 4.0–4.5 (p)
Polyaniline (PAn)		1.0	295	3.0–4.0
Polypyrrole (PPy)		0.33	136	3.0–4.0
Polythiophene (PTh)		0.25	82	3.0–4.2

Figure1.13. Various kinds of conducting polymer and its properties.[17]

The merit of conducting polymer is light weight and not expensive and easy to process. When it applied to active material for batteries, electric conductivity and redox activity are improved. However, energy density, cyclability and coulombic efficiency show low performances. It has been used as electroactive materials and conduction additive for rechargeable batteries.[43-44]
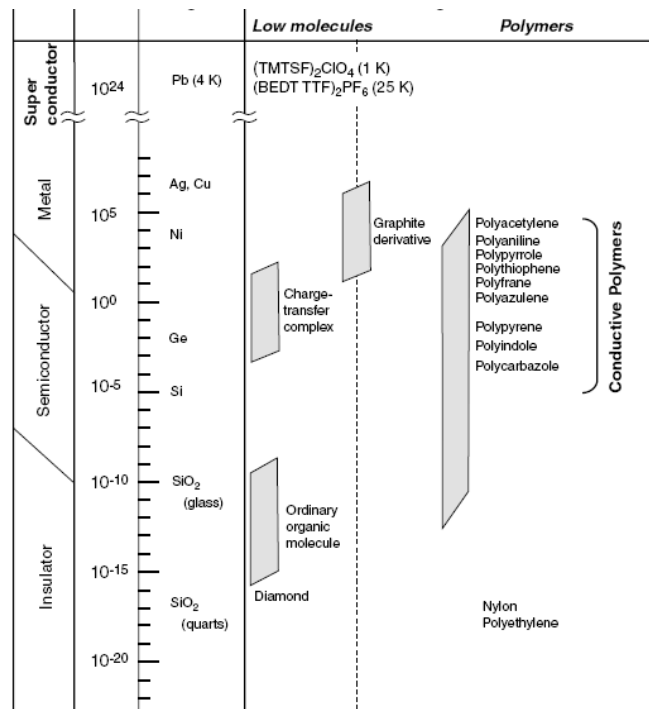

FIGURE 16.1   Conductivity of various inorganic and organic compounds and materials.

Figure1.13. Conductivity of conducting polymers and the other materials.

1.2.3. Free radical compounds

Radical is unpaired electron in molecular. Compared to occupied electrons, radical is unstable position. The polymer having radical site in polymer is radical polymer that is also unstable and reactive property.[45-46] Radical polymer is composed of two parts which are pendant group and polymer backbones.
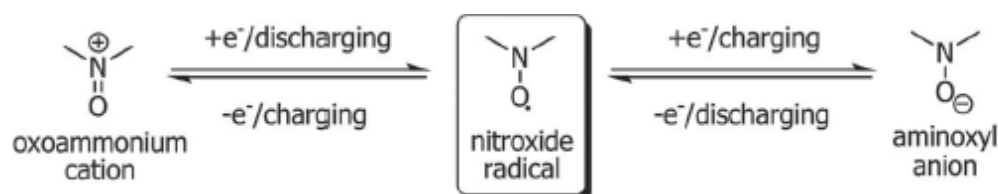
Figure1.14. Redox mechanisms of nitroxide radical compounds.

In pendant group, there is a redox reaction site where reduction/oxidation reaction occurs. As pendant group of free radical compounds in organic electrodes, nitroxyl and phenoxyl group are used a lot typically that are less reactive in unpaired electrons. About active materials, appropriate reactive degree is needed. Not too much and little. Radical electron is originally reactive, so among them less reactive pendant should be used to control the degree of it such as nitroxyl and phenoxyl group (**Figure 1.15**). These groups have conjugated structure which has resonance effect and substituent groups have sterically hindered effect also.
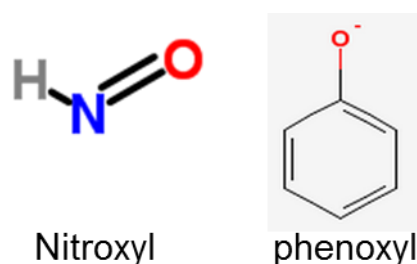
Figure. 1.15. Schematic diagrams for nitroxyl and phenoxyl strucures.

Commonly nitroxyl radical compounds are more commercialized nowadays in papers then the **Figure 1.15** explains the redox mechanism of it. Generating radical species, reduction/oxidation occurs in nitroxide-based polymers. In reduction state, nitroxide group gets electrons then become oxoammonium cation that is positively charged. In oxidation state, it loss electrons then become

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aminoxyl anion which is negatively charged.[47] These radical polymers could become both positively and negatively charged state (Figure 1.14). Using n-and p-doping mechanism, bipolar redox-active radical polymer was applied to rechargeable system (Figure1.16).[48] Positively charged radical polymer had redox reaction at 1.4V and negatively charged radical polymer had redox reaction at -1.0V which was applied to cathode and anode respectively. Using the potential gap between them, batteries could be made in same materials.[49]
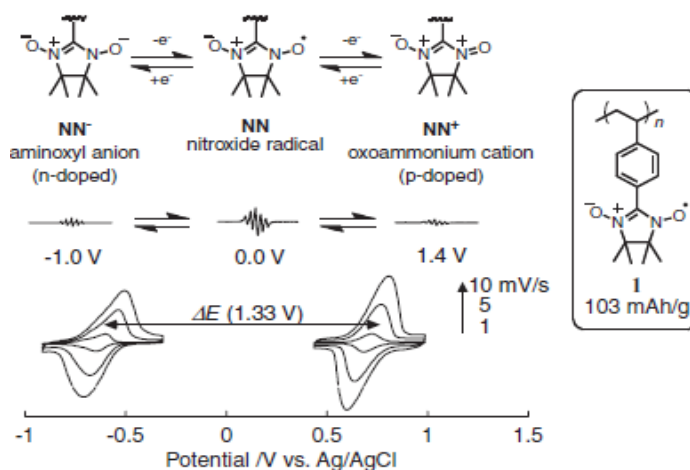
Figure1.16. Redox reaction mechanisms and cyclic voltammograms of nitroxide radical active materials.[48]

Polymer backbones act connecting pendant groups which should achieve properties of insolubility because organic electrode materials are usually dissolved in electrolytes. To improve ionic conductivity, affinity to electrolyte is important. Considering main two factor and others like process ability and mechanical strength, PMA (poly methyl acrylate) polymeric backbone was selected a lot in papers. Among pendants group, TEMPO (Poly 2,2,6,6-tetramethylpeperidinyloxy-4-yl methacrylate) was used a lot as nitoxoxide group **(Figure 1.17)**. In 2002, using TEMPO with PMA backbone, nakahara made organic batteries.[50] Theoretical capacity of TEMPO was 111mAh g-1 and redox reaction plateau was 3.5V (versus li/Li-1). As battery electrode materials, TEMPO had high rate capability and good cyclability due to its fast kinetics.[51-56] However poor electric conductivity of polymers caused adding 50% carbon to electrode composite. To improve conductivity, single-walled carbon nanotubes (SWNTs) were added into TEMPO electrode composite as conductive agents.[57]

Stable radicals used as redox-active pendant groups

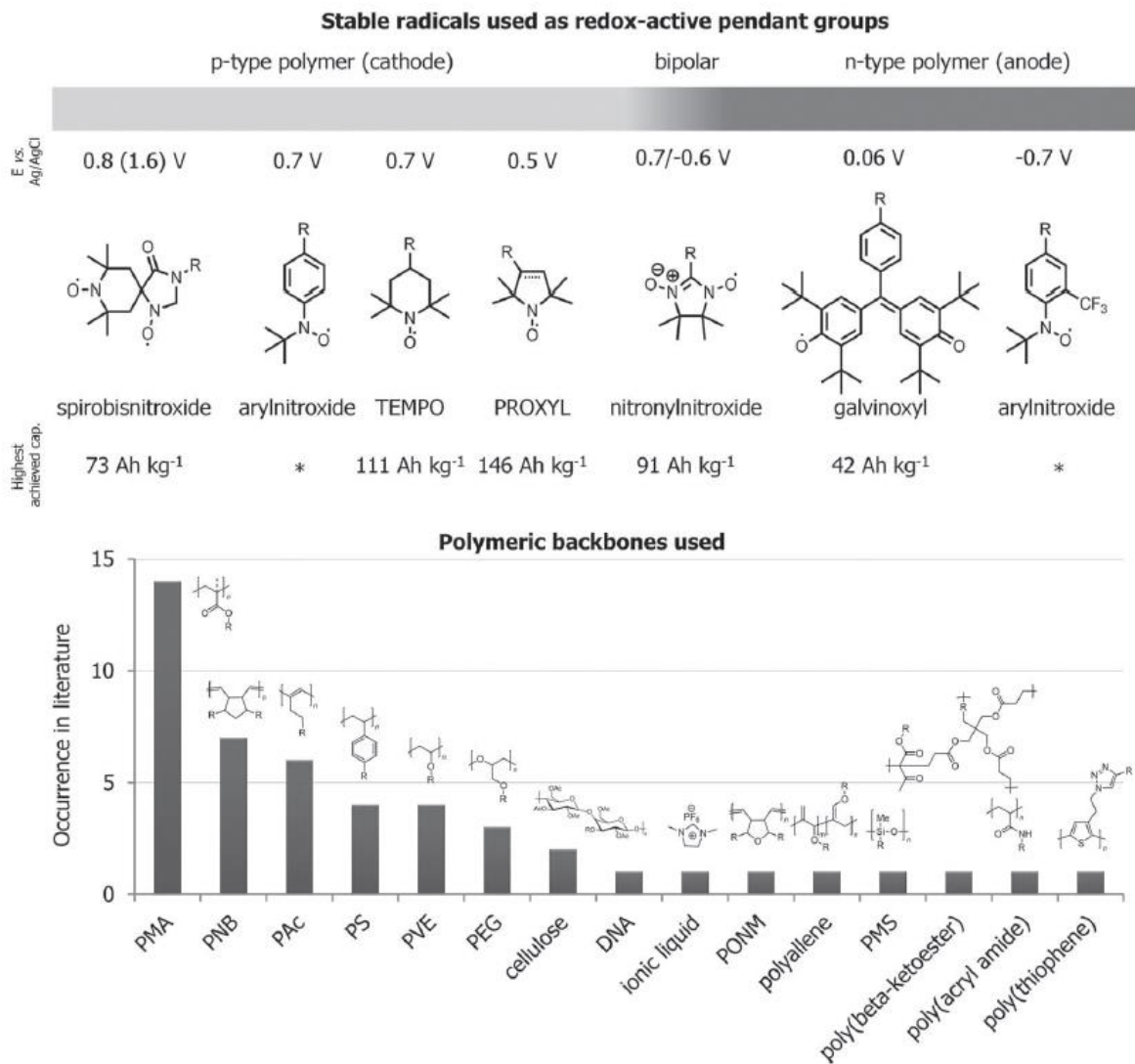|	p-type polymer (cathode)				bipolar	n-type polymer (anode)	
E vs. Ag/AgCl	0.8 (1.6) V	0.7 V	0.7 V	0.5 V	0.7/-0.6 V	0.06 V	-0.7 V
	spirobisnitroxide	arylnitroxide	TEMPO	PROXYL	nitronylnitroxide	galvinoxyl	arylnitroxide
Highest achieved cap.	73 Ah kg^{-1}	*	111 Ah kg^{-1}	146 Ah kg^{-1}	91 Ah kg^{-1}	42 Ah kg^{-1}	*

Polymeric backbones used

Figure1.17. Stable radical pendants and backbones used as redox-active materials.[16]

1.2.4. Carbonyl compounds

The carbonyl compound is last material in organic electrode materials which contain carbonyl group (C=O) in functional group of polymer. In carbonyl group, redox reaction occurs. There is a mechanism of redox reaction. One electron goes into carbonyl compounds then oxygen atom gets negatively charged where carbon-oxygen double bonds become single bonds. Lithium ions naturally stick to anionic oxygen to compensate charged state. When oxidizing, anionic oxygen lose electrons and become carbon-oxygen double bond again. Also, lithium ion is out of carbonyl compounds. In the presence of R group which is stabilizing role in molecule, the carbonyl compounds have reversible one-electron reaction. Quinone-type structure which has two carbonyl groups with aromatic molecule has reversible two-electron reaction. Each carbonyl group undergoes redox reaction respectively.[58-59] Enhancing structural stability for adding aromatic molecule, Quinone structure has been popular in carbonyl compounds electrode materials.[60-68]
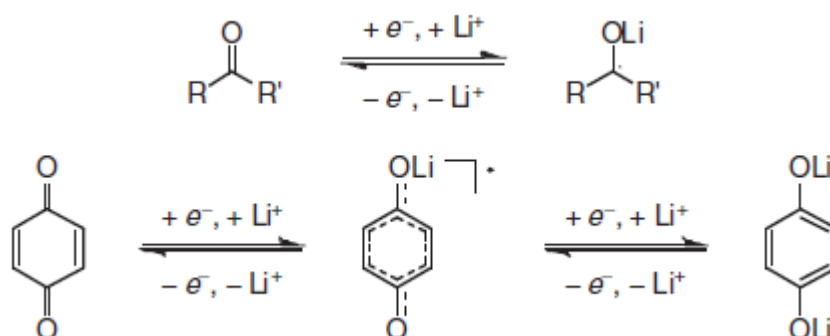

Figure1.18. Redox mechanism of carbonyl compound and quinone group.

Small organic molecules of carbonyl compounds such as quinone and dianhydried group have appropriate capacity and energy density. However, organic molecule is dissolved into electrolytes causing capacity fading and bad cycle performance. To complement dissolution of molecule, solid and polymer electrolytes were applied to batteries system though it did not achieved complete capacity performance. Organic molecules were synthesized to organic polymers to prevent dissolution problem. The main merit of organic polymers of carbonyl compounds are improving insolubility for electrolytes resulting in high cyclability, rate capability and coulombic efficiency. The polymeric backbone connects each molecule and make enormous massive which is not easily dissolve. The demerit of these polymeric carbonyl compounds is also exists. There is charge repulsion interaction between pendant units and fundamental insulation of polymer making low conductivity.

Among quinone type structures, anthraquinone based polymer was appled to cathode materials for rechargeable lithium batteries **(Figure 1.19)**. Polyanthraquinone (PAQS) was synthesized from dichloroanthraquione (DCAQ) in NMP solution at 200℃. Compared to organic molecules, PAQS had high coulombic efficiency cyclability and rate capacbility in battery performances.[63]
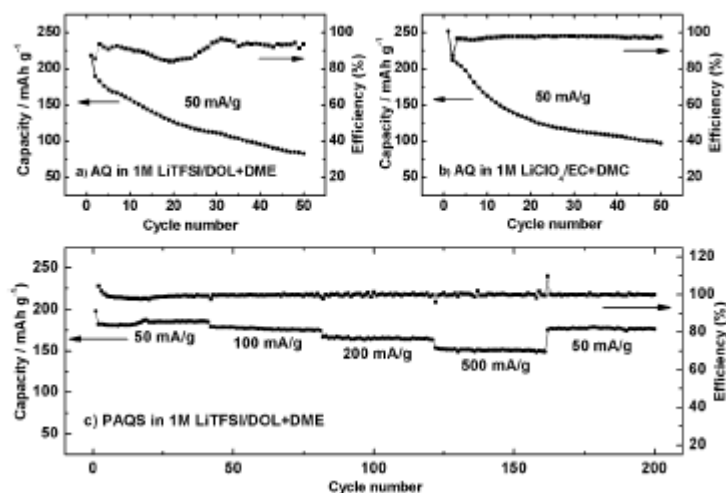

Figure 1.19. Discharge capacity of AQ and PAQS.[63]

In recent, there have been a lot of papers about carbonyl compounds as cathode materials for stable cyclability and rate capability in rechargeable batteries. The main problems of it are insolubility and conductivity of polymer. To improve these properties, many trials have been done in three directions about molecular engineering, nanostructured organic materials and quasi-solid electrolyte. In molecular engineering, Yanliang Liang putted other hetero atoms such as oxygen, sulfur, nitrogen atoms into anthraquinone materials **(Figure 1.20)**.[69] That heteroatom molecular engineering changed the LUMO and HOMO energy causing difference of redox voltage, morphology and ion diffusion. In a graph of reduction potentials of materials, PID and BFFD polymer had highest point which means LUMO energy. Discharge capacity showed DFFD and PID was best among other rused organic compounds. Also when looking at SEM image, the mixture of BFFD and PID was well blended together that showed interpenetrating structure. In other hands, BDTD and AQ was not mixed crystalizing itself like particles and rods. Electronic/ionic conductivity performances of BFFD and PID went up. Finally, the important properties in batteries were affected by heteroatoms in carbonyl

groups. This paper showed that we could control these properties by synthesizing organic carbonyl compounds.
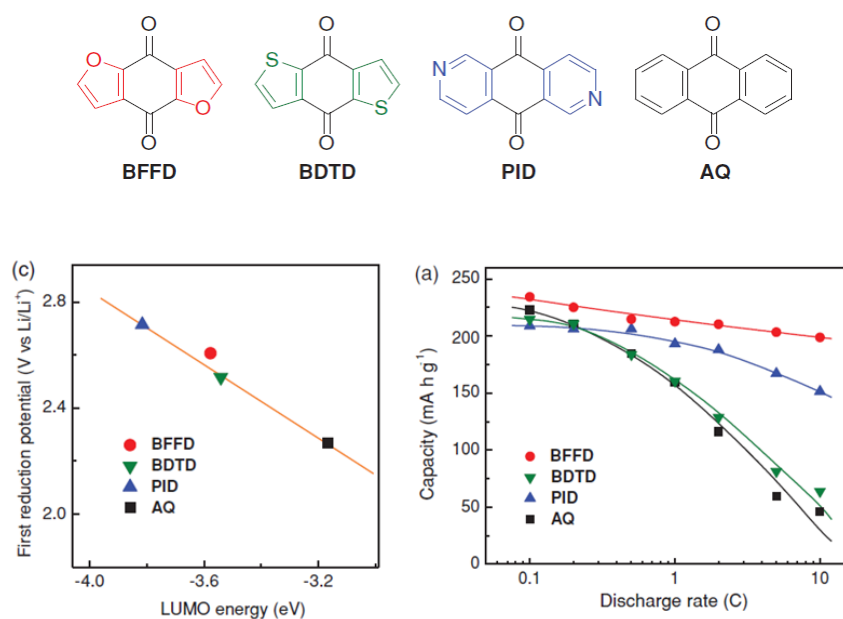
Figure1.20. Molecular structures of fused aromatic compounds, reduction potential and discharge capacity of them.[69]

Carbonyl molecules were made to nano-size structures such as nanosheets and nanoparticles.[70] The organic molecules, DHTPA had redox reaction of both negatively charged state and positively charged state at 0.8V and 2.6V respectively with 4 electrons movement. The bulk structure of DHTPA was changed into nanosheet and nanoparticles. **Figure 1.21** shows that the capacity performance of nanosheets molecule was best because nanosheets could get numerous active sited in structure then facile electric/ionic transfer was possible.
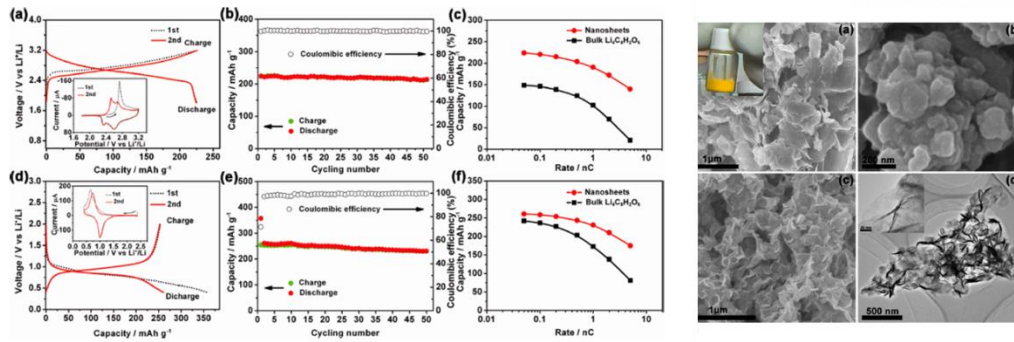
Figure1.21. Electrochemical performances and SEM images of nanostructures in DHTPA.[70]

The liquid electrolytes in carbonyl cathode electrode batteries were replaced to gel polymer electrolytes **(Figure 1.22)**.[71] Calix materials were used which was phenol based oligomers. When it was oxidized, 8-electrons fully have redox reaction with low hindrance of quionone molecules. Gel polymer electrolytes were that PMA (poly methacrylate) and PEG (poly ethylene glycol) hybrid electrolytes. Gel polymer electrolytes were PMA and PEG hybrid electrolytes. Polymer chain segments is mobile that lithium ion was solvating. PMA/PEG gel electrolyte was 20 folds low conductivity compared with liquid electrolyte. But still it could be used in rechargeable batteries. The redox potentials was 2.64V (versus Li/Li$^+$). The capacity is 422mAh g^{-1} and coulombic efficiency is over 95% in 100cycles at 0.2C.
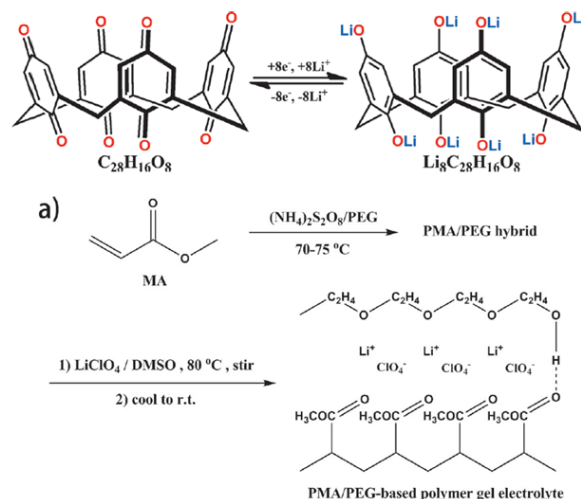
Figure 1.22. Calix structure and PMA/PEG hybrid electrolytes.[71]

Summarizing organic electrode compounds, organosulfur materials have high capacities about 300-800mAh g^{-1} and low cyclability and rate capability. Radical materials have good rate capability and low capacity. Finally carbonyl materials have stable cycling and low rate capability. Most organic compounds are electric insulators which need 30-80% conductive carbon. Dissolution of active materials in electrolytes causes capacity fading. Among organic electrodes compounds, the true material satisfying all of high energy/power density and cycling stability simultaneously has not been existed so far. To find special advantage compared to inorganic electrode material, we need to investigate these polymers by synthesizing functional groups in the future.

Figure 1.23. The voltage and specific capacity windows for organic electrode materials.

1.3 Poly vinyl carbazole (PVK)

One of the organic electrode polymer is non-conjugated redox polymers. Poly (*N*-vinylcarbazole) (PVK or PVCz) is a series of s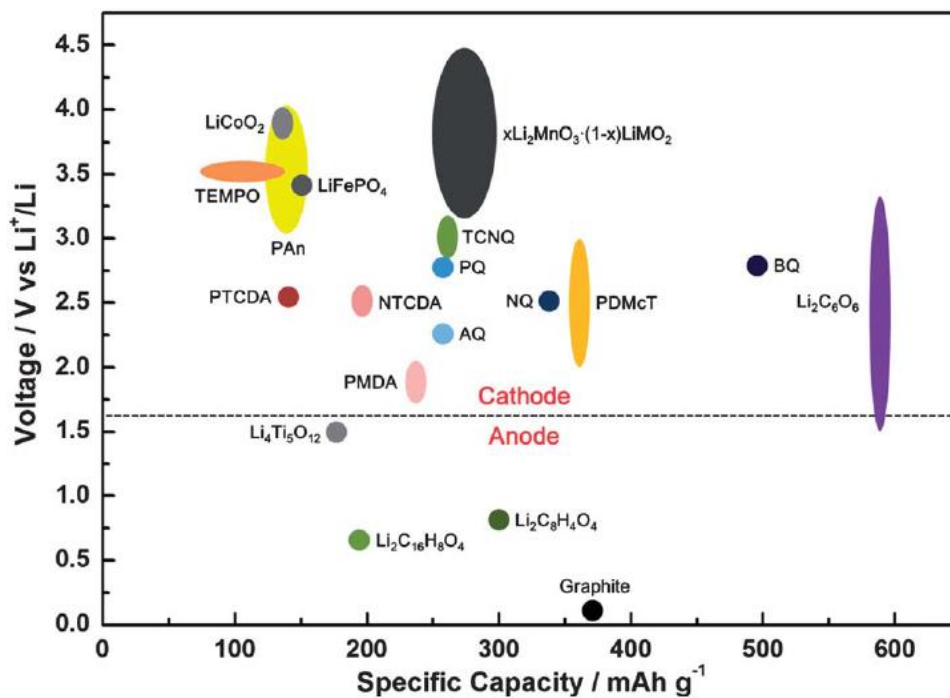everal non-conjugated pendant-type polymers. It has non-conjugated alkyl backbones and redox point of carbazole pendent. PVK is a photoconductive polymer among several pendant-type polymers. In the carbazole moiety, there are many π-bonds of benzene ring that can be stacked with each polymer.[72] The structures of PVK is very stable. And between π-bonds, there is conduction in PVK polymer, so it has fast kinetics. Also PVK has reduction/oxidation reaction in carbazole which is appropriate to positive organic material in rechargeable batteries (**Figure 1.3.1**). PVK is not dissolved in electrolyte in conventional Li-ion batteries. Theoretical capacity of PVK is 138mAh/g and the redox potential is 3.7V vs Li/Li$^+$. Attractive organic materials for lithium-ion batteries at positive electrode. 90 percent of carbarzole pendant undergo redox reaction.
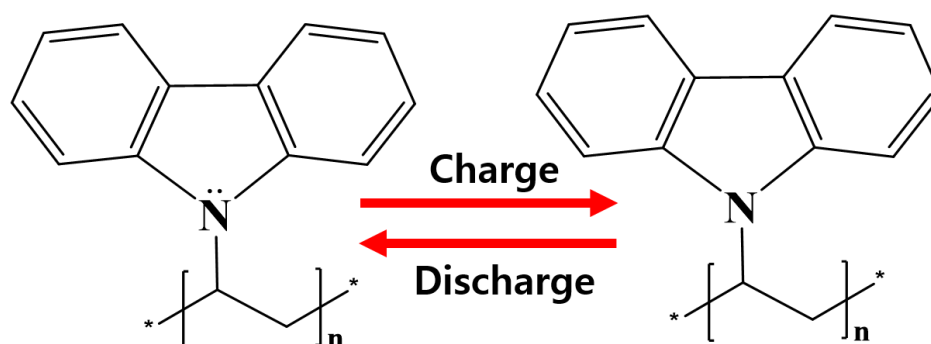
Figure 1.3.1. PVK redox mechanism.

In 2012, Masaru Yao recognized the electrochemical property of PVK polymer and used it as positive electrode materials applied in rechargeable lithium batteries.[72] The cycle-life performances are stable and show 120mAhg^{-1} with 20mAg^{-1} current density (**Figure 1.3.2**). Also, PVK was accessed as binder in LFP cathode electrode due to adhesion and cohesion property of PVK.
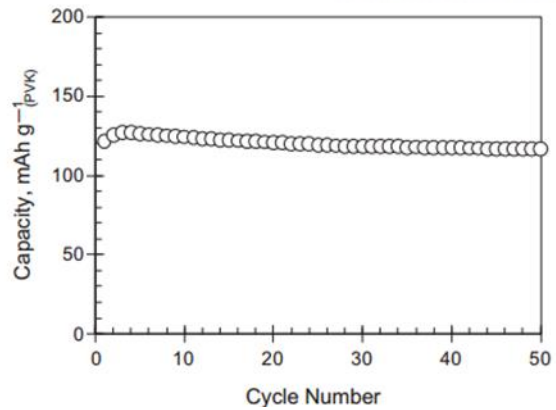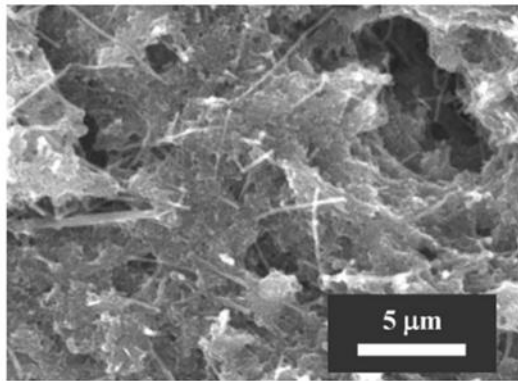
Figure 1.3.2. The SEM image of PVK and cycle-life performance of PVK electrode.[72]

In 2014, using PVK as cathode in Li-ion batteries, Jieun Kim changed PVdF binder to PEDOT which has electronic conductivity itself.[73] For better performance in batteries, ionic pathway and electric pathway should be favorably connected which was satisfied by using PEDOT polymer. The active site of PVK polymer was well blended with PEDOT polymer without binder and the single lithium-ion cell achieved high-rate capacity. **Figure 1.3.3** shows the capacity performance of electrodes using 1% PEDOT was superior to the 10% PVDF one at 100C-rate.
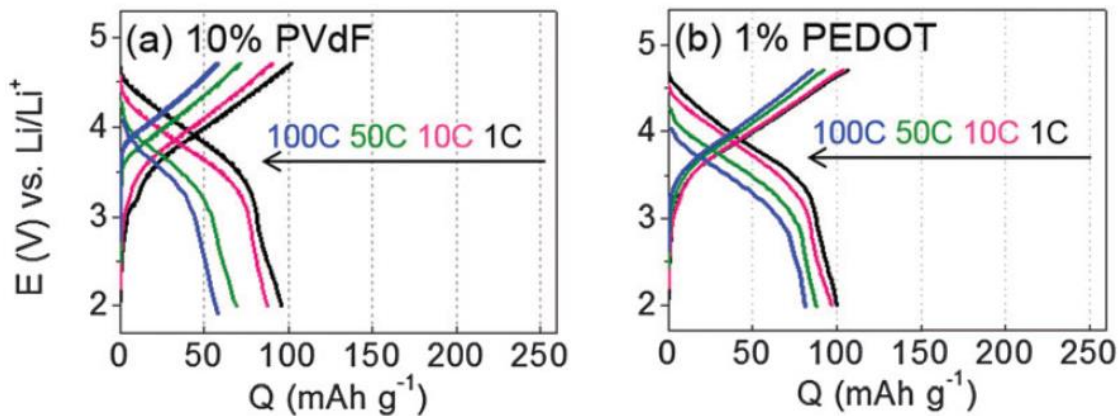
Figure 1.3.3. The capacity of using (a) 10% PVdF binder and (b) 1% PEDOT binder in PVK electrode.[73]

1.4 Spray method
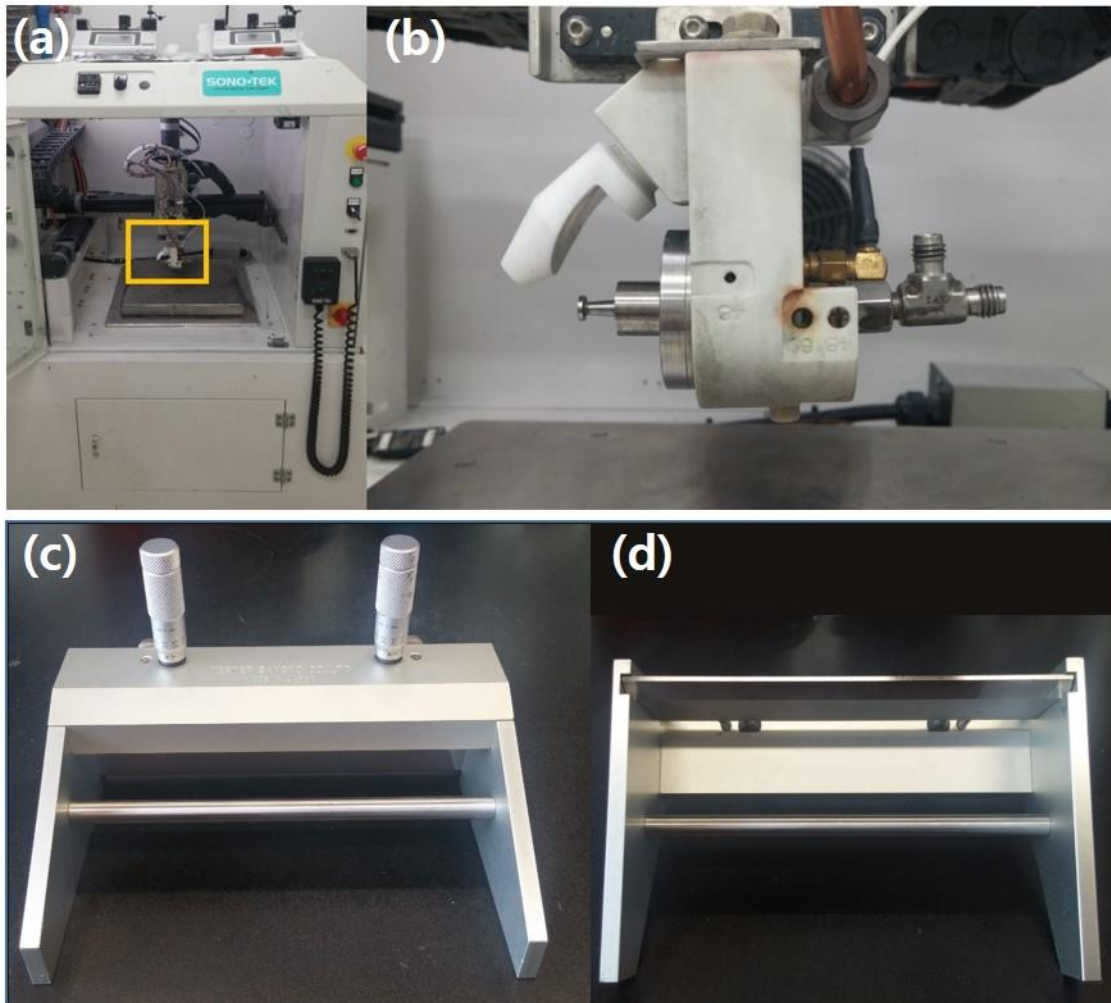
Figure 1.4.1 The picture of (a), (b) spray method and (c), (d) blade method.

Two techniques were selected for fabricating electrodes. First is doctor blade that is conventional method for lithium ion batteries electrodes. Second is spray deposition that equipped ultrasonic machines. Doctor blade method is simple process to fabricating electrodes and could get the flat surface with some thickness. Spray deposition is easy method to make various surface of electrode like curved surface or fabric. Controlling the thickness is possible by changing cycle number in equipment. With sonic machines, the solution would be more miscible **(Figure 1.4.1).**

2. Experimental

2.1 Cell preparation

Composite were prepared as working electrodes of cathode by doctor blade and spray equipment. Electrode mixture were composed of PVK as active material, PVdF or PEDOT:PSS as binder and Super P as conductive agents which were dissolved into *N*-methiyl-2-pyrrolidone (NMP) solution. The composition ratio of PVK, PVdF and carbon black was 50 : 10 : 40 while the composition ratio of PVK, PEDOT:PSS and carbon black is 50 : 1: 40. In spray equipment, liquid mixture were contained in syringe and sprayed out with constant speed of flow rate on Al foils. The cycle number of spray method was 30cycles with 0.3mg g^{-1} active materials mass. Flow rate of solution in syringe to spray nozzle was 150ul/min. The temperature of bottom heater below Al foils was 120℃. By doctor blade coater, electrode mixture which had viscous property was pasted on Al-foils and setting thickness of doctor blade was 130um. Electrode mixture dried under vacuum at 120℃ for 2hr.

After making each electrodes, half coin cells were manufactured by piling a working electrode, separator and lithium metals as counter electrode in these orders. 1M $LiPF_6$ in ethylene carbonate/dimethylcarbonate (1 : 1 v/v EC : DMC) was used for electrolyte in coin cells.

2.2 Electrochemical analysis

By using a potentiostat, cyclic voltammogram and impedance spectroscopy were analyzed (Biologic, VMP3). The coin cells were galvanostatically cycled between 2.0V and 4.7V voltage range versus Li/Li+ (WonAtech, WBCS3000). The current was 1C that was defined as 120mA g^{-1} based on active material mass.

2.3 Physical properties

The electrode morphology was observed by scanning electron microscopy (SEM; Hitachi, S-4800). Conductivities of composite were measured by four-point-probe equipment (Dasol, Rs8-1G). Thickness of composite was measured by Vernier caliper.

3. Result & Discussion
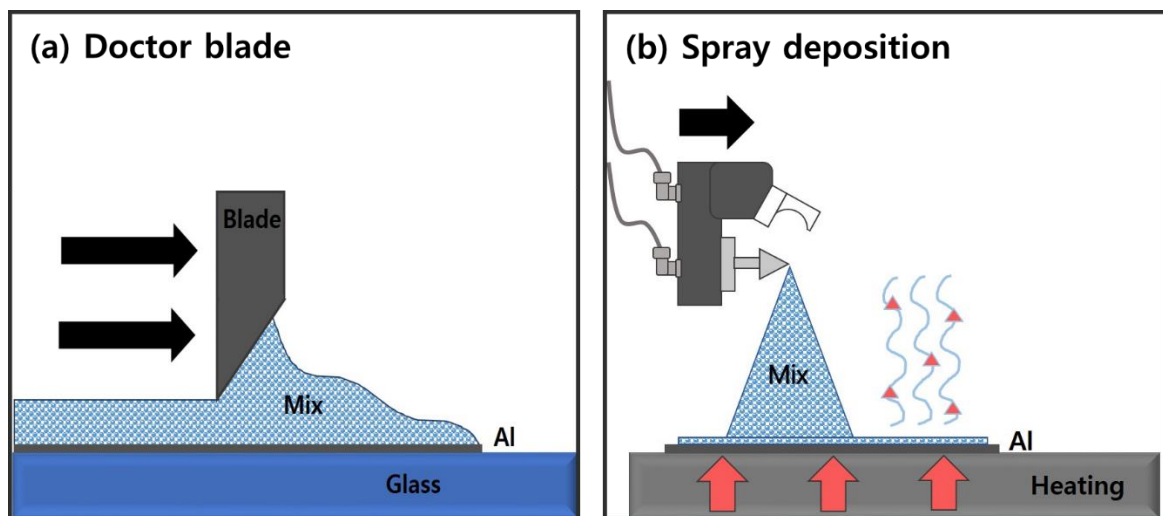
Figure 3.1. Schematic illustrations of fabricating the electrodes by (a) Doctor blade and (b) Spray deposition.

Figure 3.1 shows schematic illustrations of fabricating the electrodes by doctor blade and spray deposition. Left figure is about electrodes making by doctor blade. Mixtures containing certain amount of solvent were pasted, when blade cut are pushed horizontally. With sharped blade cut, doctor blade make surface of mixtures flat. After fabricating, the electrode was put into the vacuum oven and dried. Right figure explains how ultrasonic spray deposition equipment make electrodes. The mixtures with low viscosity went into the one tube and reached the ultrasonicated point where the mixtures blend together well. Then getting out of the tube, the liquid of mixtures sprayed with tiny droplets (=50um) on the current collector. With nitrogen gas pressure, force was added vertically. Solvent of the droplets were rapidly evaporated during the time of flight as well as when they met heated current collectors. The components originally included in the droplets were densely packed on the current collectors.
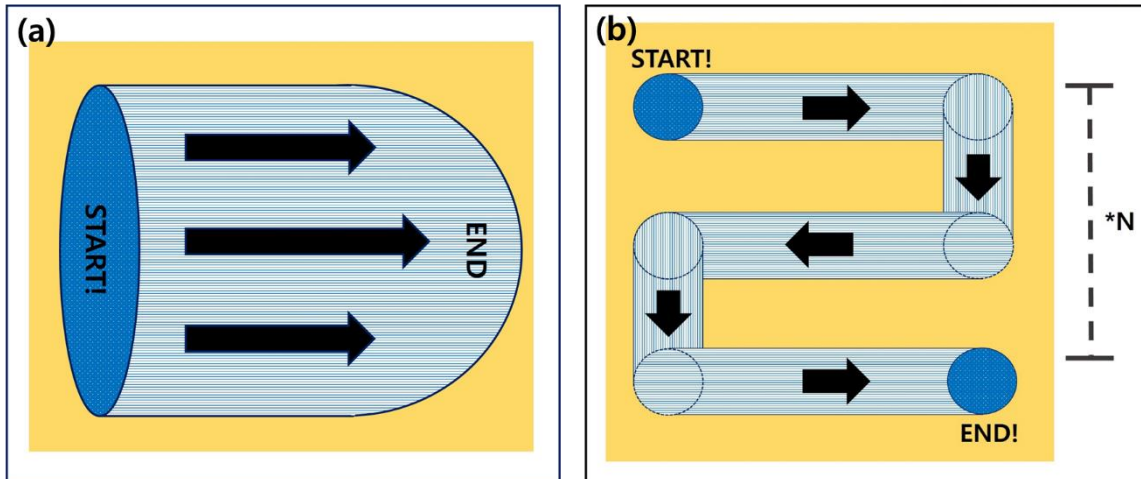
Figure 3.2. The top view of motion when electrode is fabricated by (a) Doctor blade and (b) Spray deposition.

Figure 3.2 indicates the top view of motion when electrode is fabricated by two different methods. First figure is the electrode using doctor blade technique **(Fig 3.2a)**. The mixture were pushed with one direction at once. In spray deposition, the nozzle of spray equipment moved like Hangeul consonant 'ㄹ' with fixed speed programmed. There is a constant thickness for each cycles due to perfect evaporation of solvent. It can be easier to estimate the thickness and loading weight of electrode which is practical compared to doctor blade. Regarding doctor blade, thickness of electrode that finish drying in vacuum oven are thinner than origin which result from both fluidity of pasted mixtures and evaporation of solvent. On the other hand, the nozzle of spray equipment moved in order of designated coordinates (X, Y, Z). The size of electrodes could be changed from small to big area. Also it can be possible to spray out the diverse surface (ex. fabrics, curved object) since force of spray deposition is vertical, not horizontal. Spray deposition can be applicable to variable substrates of electro equipment.
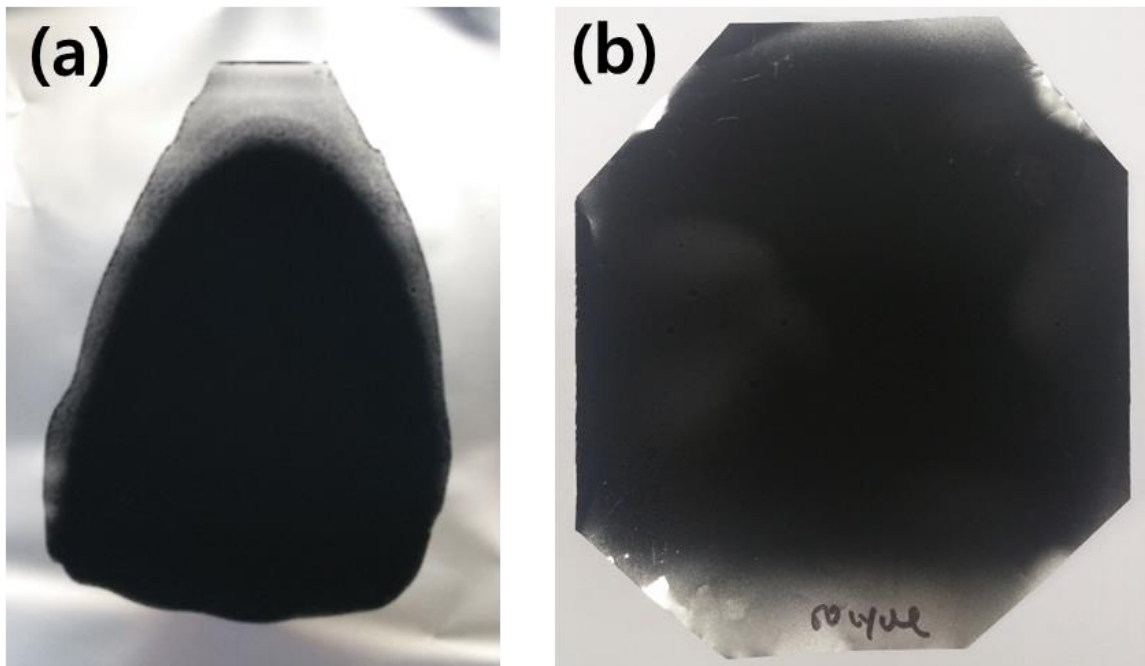
Figure 3.3. The pictures of electrodes by (a) Doctor blade and (b) Spray deposition method.

This is the picture of fabricated electrodes (**Figure 3.3**). Electrodes done by both spray coating and blade technique was well fabricated. It seems that the linear polymers of PVK and PEDOT:PSS or PVDF got tangled each other[ref]. Especially the polarity of respective polymer are same which means all of these polymers has polar property. Solvent of electrode was NMP that has a polar property and it dissolved PVK, PEDOT and PVdF. As we know 'like dissolve like' indicate that NMP or polar solvent dissolved polymers and then polymer also had polar property. About PVK, an amine atom pulled the other atoms around, making a difference of electronegativity between them. In PVdF, double fluorine atoms attracted highly a carbon atom and then asymmetry was occurred in that polymer unit, resulting in a big difference of electronegativity or polar property (Figure 3.4). Similarity, PSS polymer in PEDOT:PSS had enormous polarity coming from drawing of SO^{3-} group. Therefore PVK polymers, PVdF binder and PEDOT, all had polar property and got high possibility to get blended together well with carbon black. Also, good adhesion property of PVK took a role to making electrodes. In addition, binder which was PEDOT:PSS or PVdF.
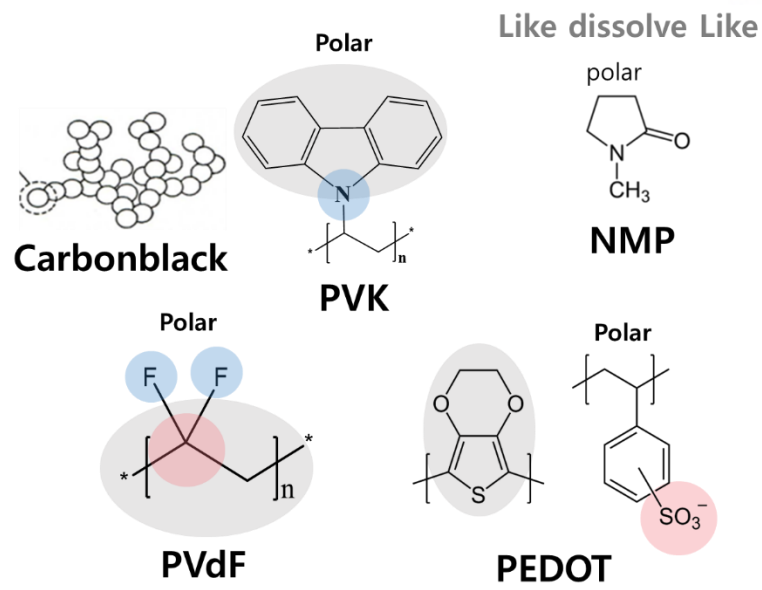
Figure 3.4. The molecular structures of polymers in electrodes composite.
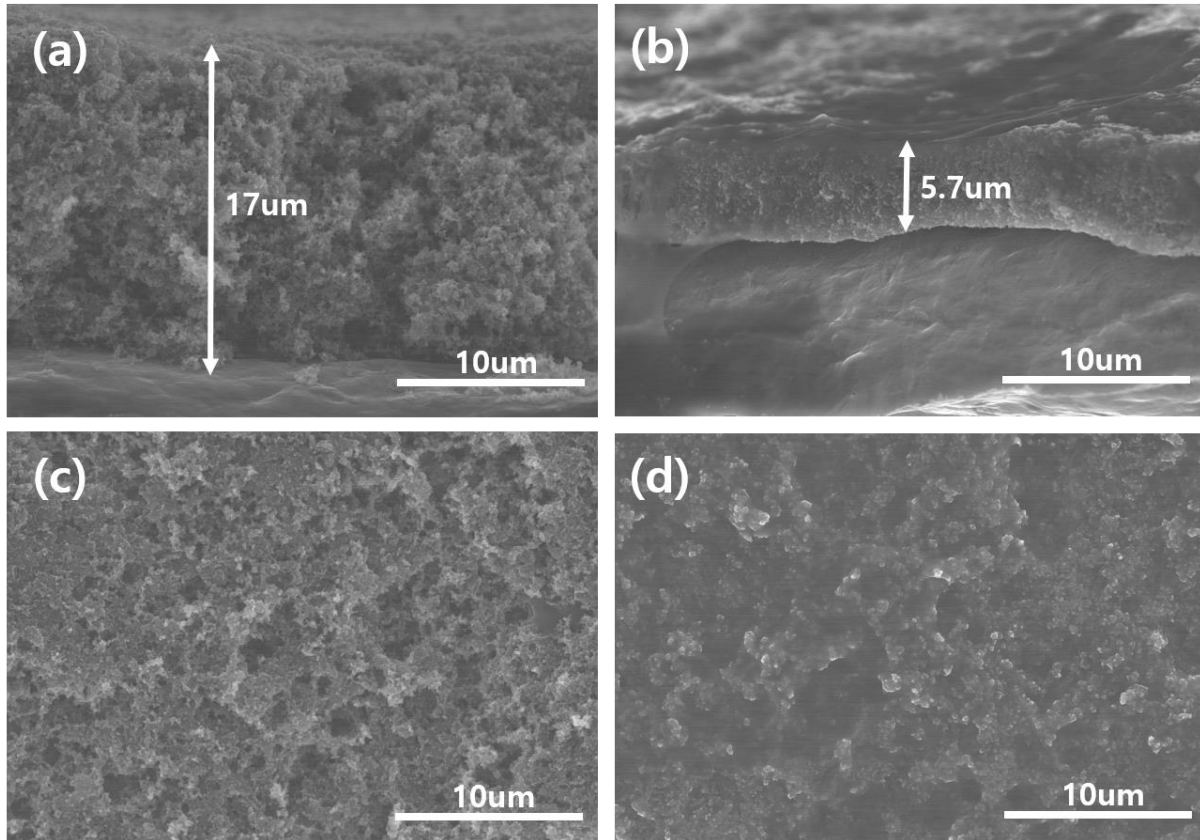
Figure 3.5. The SEM image of blade electrodes (a), (c) and spray electrode (b), (d) using PVdF binder.

We can compare morphology of composite on electrodes **(Figure 3.5)**. The thickness by spray deposition is nearly three times thinner than doctor blade. As you can see from the pictures, electrode composites using doctor blade have a lot of pores in inner parts while sprayed composites are densely stacked with little pores. About a view on adhesive property, electrode composite by spray deposition is easily stick to Al foil as well as composite each other. The adhesion have different causes. One of them is miscibility of components that is cohesion. The other is spacious contact area of binder with current collector and composites that is adhesion. When looking at the interface of Al foils and composites, spraying electrode have large contact points between them. However blading electrode have less contact points contrasting to spraying one due to lot of pores. About composites to composites, this could be equally applied. Spraying composite electrode has more strong interaction between composites than blading one.
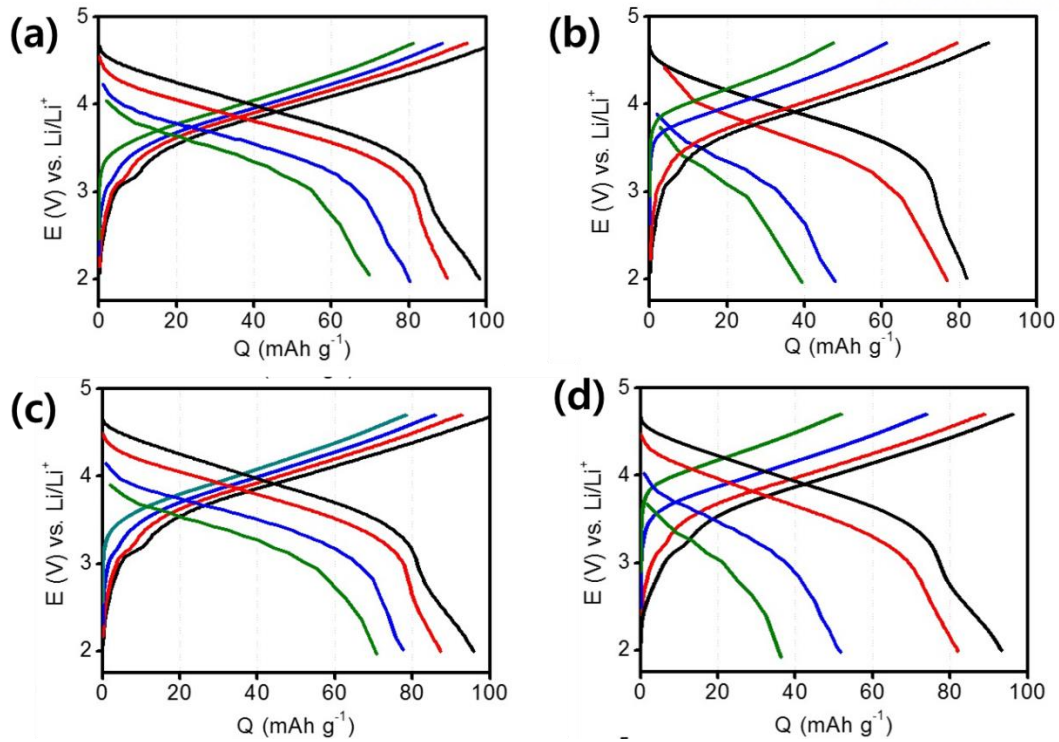
Figure 3.7. Gravimetric capacity of (a) Blade electrode, (b) spray electrode using PVdF and (c) blade electrode, (d) spray electrode using PEDOT.

When looking into views on gravimetric performance of potential profiles, we could explain the results with the morphology of electrode composites (**Figure 3.7**). About using PVdF binder, the capacity of blade electrode was 100mAh g^{-1} at 1C and 70mAh g^{-1} at 100C while the capacity of spray electrode was 82mAh g^{-1} at 1C and 40mAh g^{-1} at 100C. The decreasing capacity percent between 1C and 100C of blading one was about 30% and spraying one is 50%. The rate capability of blade electrode was better than spray one. About using PEDOT:PSS, the capacity of blade electrode was 98mAh g^{-1} at 1C and 72mAh g^{-1} at 100C while the capacity of spray electrode was 95mAh g^{-1}at 1C and 39mAh g^{-1} at 100C. The rate capability of blade electrode was also better than spray electrode when using PEDOT:PSS. The difference in performances results from two factors that were electronic pathway and ionic pathway. For a complete performance in batteries, electronic pathway and ionic pathway go together. However in our experiments, the conditions for electronic pathway were sufficient, since the composition ratio of conductive material, carbon black was forty percent. Electronic conductivity of electrode composites was optimized. Also, PVK polymers had intrinsic good kinetics due to pie-pie interaction when carbazole moieties were piled up. Through pie-pie

36

bonds, electrons moved fast among polymer chains. The affordable reason for bad performance at 100C was ionic pathway. The spray electrode composites was three times dense so it had little pores in composites. While an hour was enough time that lithium ion could move into both composite that was the condition of 1C. 36 seconds was very short time for lithium ion to move into both composite that was the condition of 100C. Especially lithium ion movement was highly limited in spay electrode composites with little pores. Ionic pathway was less developed in spray electrodes for poor pores structure. Therefore, the rate capability of blade electrode was higher than spray electrode.
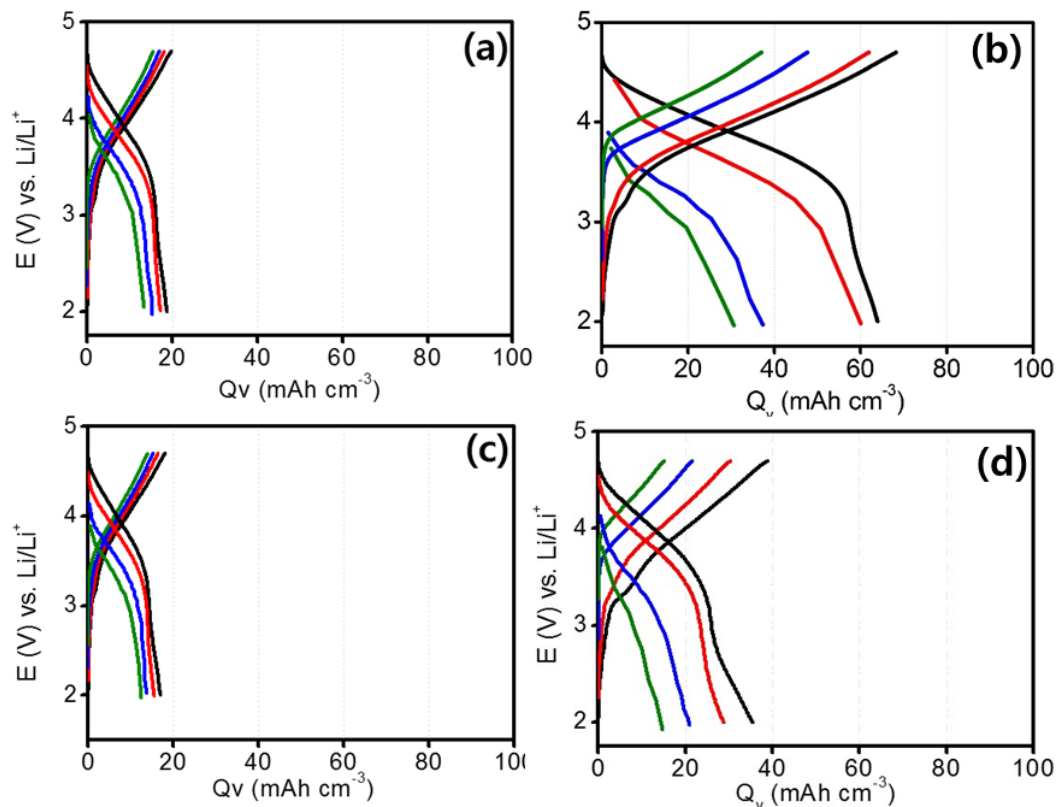
Figure 3.8. Volumetric Potential profiles at 1C, 10C, 50C and 100C discharge rates (a) PVDF-Blade (b) PVDF-spray (c) PEDOT-Blade (d) PEDOT-spray. Active material density (d_A) = 0.3 mg cm2.

When calculating capacity as volumetric value, not gravimetric values the performance data were exchanged between them. **Figure 3.8** shows potential profiles of each samples tested at various C-rates in volumetric capacity. For PVDF binder electrodes, the volumetric capacity of blade electrode was about 20mAh cm^{-3} at 1C while the spray electrode was 64mAh cm^{-3} at 1C. The volumetric capacity performance of spray electrode was three times bigger than blade electrode at 1C. Even at 100C, spray electrode was nearly doubles compared to blade electrode. Likewise for

PEDOT:PSS, the volumetric capacity of blade electrode was near 20mAh cm^{-3} at 1C while spray electrode was 38mAh cm^{-3} at 1C. The volumetric capacity of spray electrode was about twice bigger than spray electrode at 1C. The thickness of spray electrode was three times thinner than the blade one and these differences of thickness value affected volumetric capacity overall in cell performance.

Capacity retention (%)
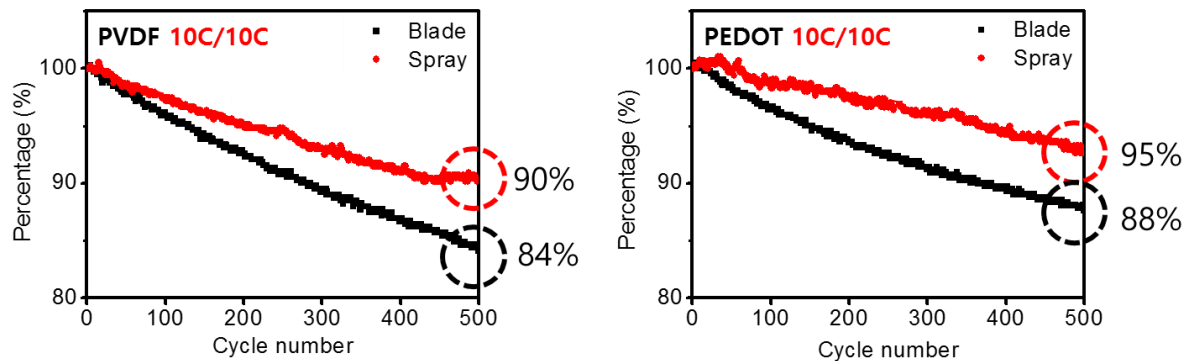
Figure 3.9. Capacity retention of electrodes using (a) PVdF and (b)PEDOT.

Figure 3.9 showed capacity retention of each electrode at 10C during 500 cycles. The speed of 10C-rate was very harsh condition for battery cycle test. In using PVdF binder, the capacity retention of spray electrode was 90% while blade electrode was 84%. The capacity retention of spray electrode was better than blade electrode. In using PEDOT:PSS, the capacity retention of spray one was 95% while blade one was 88%. Also for PEDOT:PSS, the performance of spray electrode was better than blade electrode in capacity retention. When using PEDOT:PSS overall capacity retention was better than PVdF binder which means PEDOT:PSS was superior to PVdF as binder. Suppose that small amount of 1wt% PEDOT:PSS in composite could be helpful to lithiation/delithiation of ions when long cycle of charging/discharging compared to 10wt% PVdF binder. Anyway total two graphs showed that spray one is better than blade one. The outcome data results from the adhesion property.
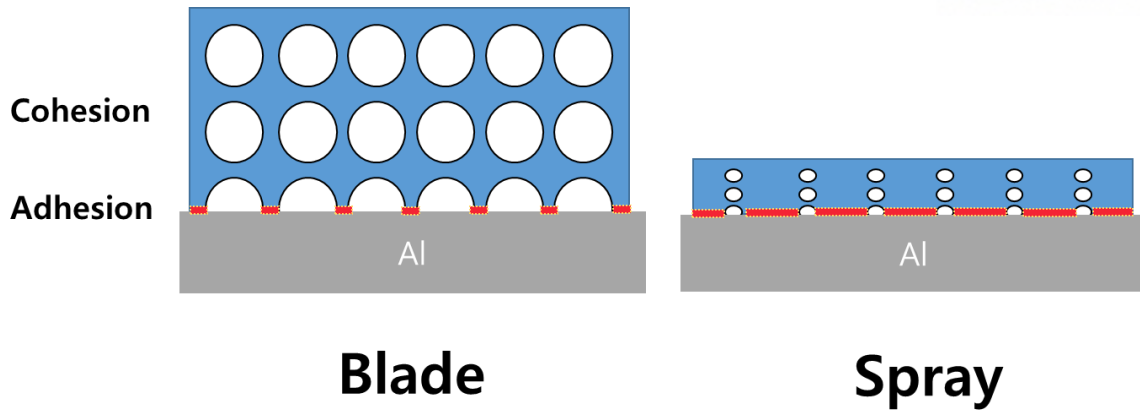
Figure 3.10. The explanation pictures of adhesion property in blade and spray electrode.

The adhesion property about polymers came from two factors. First was interfacial contact area and second was intrinsic adhesion force of polymer contents itself according to its functional groups. In **Figure 3.10**, the adhesion data between spray and blade electrode was compared, in same binder which means that all components in each electrode are same. The intrinsic adhesion force which came from the polymer was same. Therefore the interfacial contact areas only made effects to adhesion of electrodes that was directly connected to capacity retention. When looking into the interface between Al current collector and electrode composites, the amount of red line in blade electrode was more than spray electrode because spray electrode had bigger density than blade one. The red line indicated interfacial contact areas between current collector and electrode composite which means interfacial contact area of spray electrode was higher than blade one. Also it means adhesion between Al current collector and composites was bigger than blade. Also among electrode composite itself that is cohesion properties, spray one was better than blade one due to the difference of its density. These good adhesive properties bound electrode components well together then caused good capacity retention at long cycle life in spray electrode.

Figure 3.11. High rate capacity from 1C to 100C using PVdF binder at (a) gravimetric and (b) volumetric capacity.

Figure 3.11 shows the rate capability on various discharged rates in cells when using PVdF binder. Figure 3.11(a) express gravimetric capacity. The decreasing rate line of gravimetric capacity was similar in both spray and blade electrode until 10C, while gravimetric point of spray one was little higher. However after 20C in graph, the decreasing rate line of spray was nearly twice bigger than blade one. Previous data already shown that less developed ionic pathway in spray electrode composites caused fading capacity at high rate. In this graph, the property of ionic pathway in spray electrode affected properly from 20C-rate point compared to the value of decreasing rate in blade one. Before 20C point, the capacity was relatively affected by electric pathway property. The limitation boundary of ionic pathway and electric pathway which made effect on capacity was 20C point in PVK cathode electrode composite of battery system.

When compared with capacity of electrodes at low rate from 0.1C to 1C, the decreasing rate was similar between spray and blade electrode which were affected by electric pathway property (Figure 3.12). In volumetric capacity, the value of spray electrode was four times bigger than blade electrodes calculating each density to gravimetric capacity.
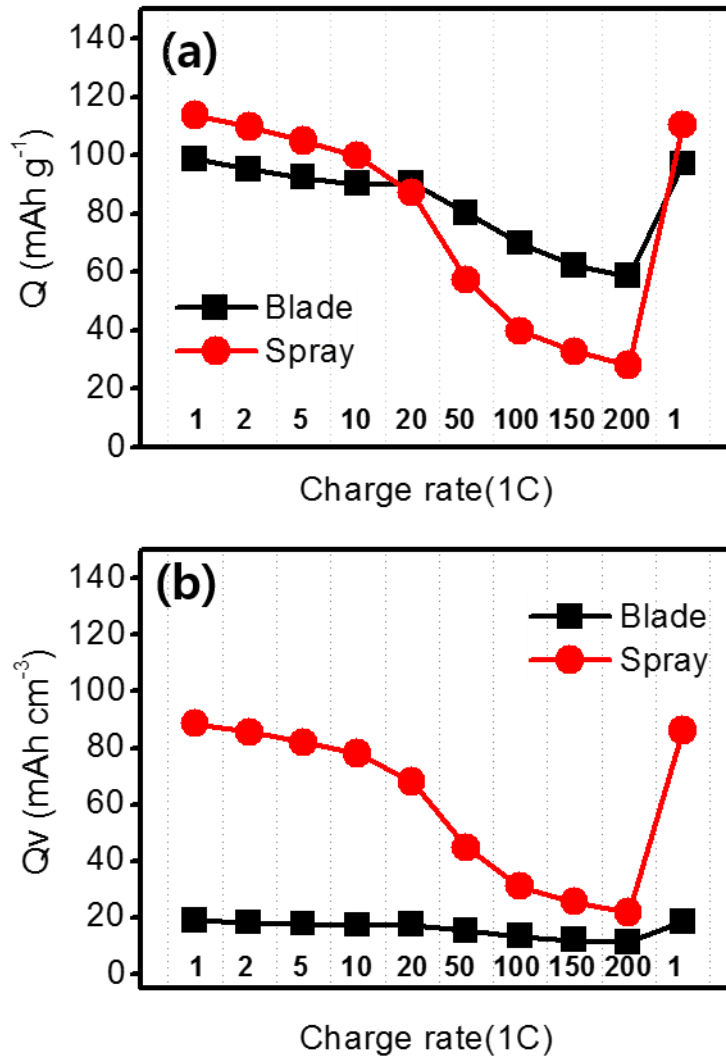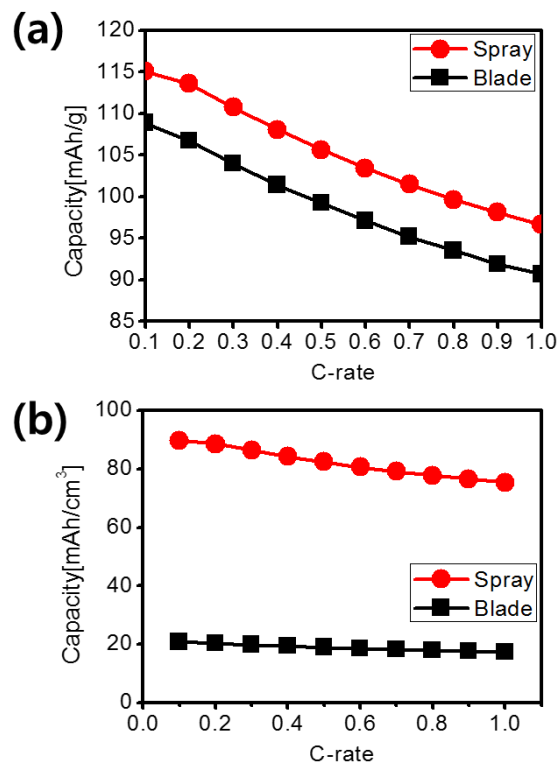

Figure 3.12. Low rate capacity from 0.1C to 1C using PVdF binder at (a) gravimetric and (b) volumetric capacity.
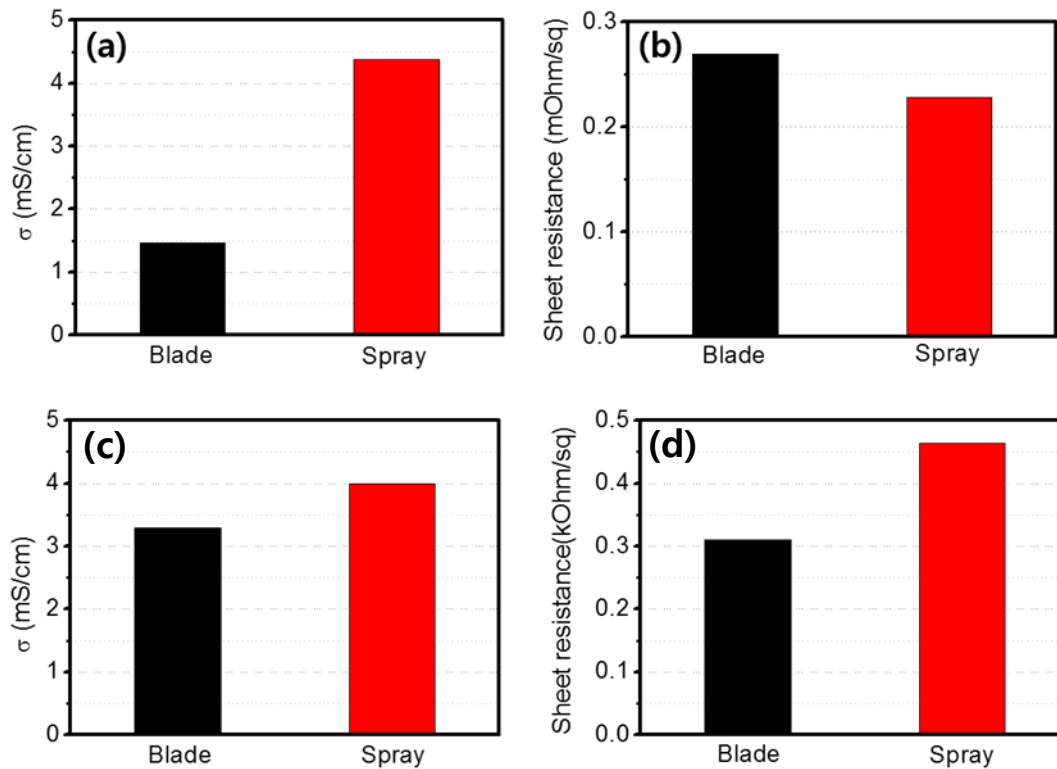
Figure 3.13. (a) Conductivity and (b) sheet resistance of PVdF binder and (c) Conductivity and (d) sheet resistance of PEDOT:PSS binder.

Electric conductivities were measured in **Figure 3.13**. The electric conductivity of spray composite was 4.5mS cm^{-1} and blade one is 1.5mS cm^{-1} for PVdF binder. The conductivity was nearly three times bigger in spray composite than blading one because spray composite three times thinner than blade composite. The factors of thickness of composites directly affect its electric conductivity. The sheet resistance of spray electrode also exceed to blade. Due to its low porosity, spray electrode had bigger density which was plus factor for sheet resistance. This was why sheet resistance of spray electrodes was better.

When using PEDOT:PSS binder, the electric conductivity of spray composite was also superior to blade composite. However, the sheet resistance of PEDOT:PSS binder electrode was different from the data of PVDF binder electrode. The PEDOT:PSS intrinsic property was added to the factors of sheet resistance in addition to its density. When using PEDOT binder to battery

electrodes, the composition ratio of PEDOT binder is optimized at one percent for its low density. The efficiency of electric conductivity decreased over one percent ratio of PEDOT:PSS after then some aggregation would occur [ref]. At spray electrode composites, PEDOT:PSS content per area were tripled due to dense packaging which made sheet resistance efficiency go worse compared to blade electrode. We estimated that over amount of PEDOT:PSS caused aggregation since PEDOT:PSS originally made thin film coating with low porosity. Also, the insulator content of PSS interrupted the PEDOT conductive pathway as the more amounts of them increased.
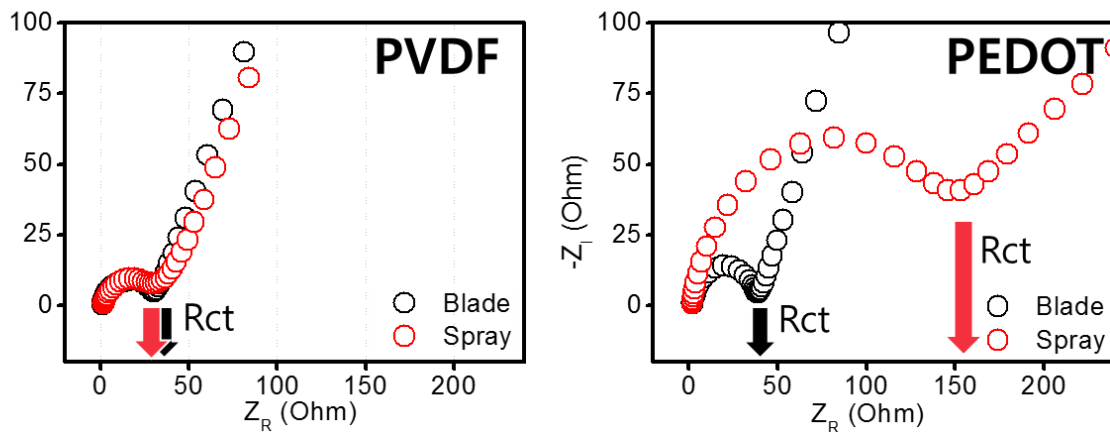
Figure 3.15. PVDF-EIS of (a) PVDF and (b) PEDOT binder.

The impedance spectra were obtained (**Figure 3.15**). The equivalent circuit model shows the electrochemical process roughly composing of Charge transfer resistance (R_{ct}), capacitance for double layer formation (C_{dl}) and diffusion of lithium ions as Warburg element (W). The semicircles indicate nonideal charge transfer. R_{ct} using PVdF binder was 40 Ohm similarly both blade and spray cell which means that the charge transfer kinetics was same between interface of electrode. Because R_{ct} originally represents charge transfer kinetic on components. Actually when there was no charging/discharging cycles, R_{ct} value of blade cell was better than spray one because ionic pathway was not build up especially dense spray cell. After several cycles charging/discharging in both cells, ionic pathway was well build up and these values got obtained which also applied to capacity value. When using PEDOT binder, R_{ct} of spray electrodes was bigger than spray one. Already said, the low density of PEDOT binder causes some aggregation in densely packed spray electrodes.
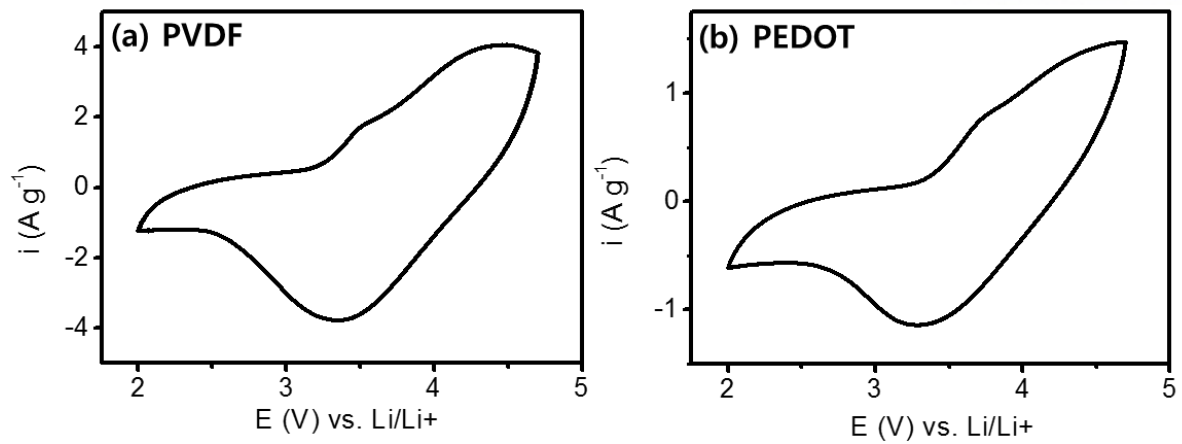
Figure 3.16. Cyclic voltammetry of (a) PVdF and (b) PEDOT.

The cyclic voltammetry was tested in coin cells **(Figure 3.16)**. The voltage of redox reaction was around 3.7V (vs. Li/Li$^+$). The current density of PVdF electrodes was bigger than PEDOT electrodes. In our experiment, PEDOT binder did not affect the conductivity of electrodes.

4. Conclusion

Poly vinyl carbazole (PVK) were used as redox-active materials. PVdF and carbon black were mixed as binder and conducting agent. Also PEDOT:PSS was used as conductive binder. Using spray deposition with ultrasonic equipment, high volumetric energy density was achieved compared to conventional blading method. Due to rapid evaporation of solvent, spray electrodes were densely packed. Compared to conventional fabrication method, spray deposition method naturally exhibited high performance in volumetric capacity. Spray method made electrode several times thinner than conventional method with same loading mass. Using these advantages, spray electrodes would be applied to various surface of electrode such as curved surface or fabrics. We expect that spray deposition method is applied to all polymer flexible batteries and conventional inorganic materials as well.

5. Refernces

1.   Marom, R.; Amalraj, S. F.; Leifer, N.; Jacob, D.; Aurbach, D., A review of advanced and practical lithium battery materials. *Journal of Materials Chemistry* **2011,** *21* (27), 9938-9954.

2.   Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D., Challenges in the development of advanced Li-ion batteries: a review. *Energy & Environmental Science* **2011,** *4* (9), 3243-3262.

3.   Scrosati, B.; Hassoun, J.; Sun, Y.-K., Lithium-ion batteries. A look into the future. *Energy & Environmental Science* **2011,** *4* (9), 3287-3295.

4.   Tarascon, J. M., Key challenges in future Li-battery research. *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences* **2010,** *368* (1923), 3227-3241.

5.   Vayrynen, A.; Salminen, J., Lithium ion battery production. *Journal of Chemical Thermodynamics* **2012,** *46*, 80-85.

6.   Park, O. K.; Cho, Y.; Lee, S.; Yoo, H.-C.; Song, H.-K.; Cho, J., Who will drive electric vehicles, olivine or spinel? *Energy & Environmental Science* **2011,** *4* (5), 1621-1633.

7.   Xu, K.; von Cresce, A., Interfacing electrolytes with electrodes in Li ion batteries. *Journal of Materials Chemistry* **2011,** *21* (27), 9849-9864.

8.   Dunn, B.; Kamath, H.; Tarascon, J.-M., Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011,** *334* (6058), 928-935.

9.   Choi, N.-S.; Chen, Z.; Freunberger, S. A.; Ji, X.; Sun, Y.-K.; Amine, K.; Yushin, G.; Nazar, L. F.; Cho, J.; Bruce, P. G., Challenges Facing Lithium Batteries and Electrical Double-Layer Capacitors. *Angewandte Chemie-International Edition* **2012,** *51* (40), 9994-10024.

10.   Bruce, P. G.; Scrosati, B.; Tarascon, J.-M., Nanomaterials for rechargeable lithium batteries. *Angewandte Chemie-International Edition* **2008,** *47* (16), 2930-2946.

11.   Hu, Y.; Sun, X., Flexible rechargeable lithium ion batteries: advances and challenges in materials and process technologies. *Journal of Materials Chemistry A* **2014,** *2* (28), 10712-10738.

12.   Nishide, H.; Oyaizu, K., Materials science - Toward flexible batteries. *Science* **2008,** *319* (5864), 737-738.

13.   Liang, Y.; Tao, Z.; Chen, J., Organic Electrode Materials for Rechargeable Lithium Batteries. *Advanced Energy Materials* **2012,** *2* (7), 742-769.

14.   Liu, M. L.; Visco, S. J.; Dejonghe, L. C., ELECTROCHEMICAL PROPERTIES OF ORGANIC DISULFIDE THIOLATE REDOX COUPLES. *Journal of the Electrochemical Society* **1989,** *136* (9), 2570-2575.

15.   Takeo Suga, H. N., Redox-Active Radical Polymers for a Totally Organic Rechargeable Battery. 5.7 ed.; American Chemical Society: 2012; pp 45-53.

16.   Janoschka, T.; Hager, M. D.; Schubert, U. S., Powering up the Future: Radical Polymers for Battery Applications. *Advanced Materials* **2012,** *24* (48), 6397-6409.

17.   Song, Z.; Zhou, H., Towards sustainable and versatile energy storage devices: an overview of organic electrode materials. *Energy & Environmental Science* **2013,** *6* (8), 2280-2301.

18.   Cho, J. S.; Sato, S.; Takeoka, S.; Tsuchida, E., Synthesis of disulfide-containing aniline and copolymerization with aniline. *Macromolecules* **2001,** *34* (9), 2751-2756.

19.   Liu, M.; Visco, S. J.; De Jonghe, L. C., Electrode kinetics of organodisulfide cathodes for storage batteries. *Journal of The Electrochemical Society* **1990,** *137* (3), 750-759.

20.   Visco, S. J.; Liu, M.; Armand, M. B.; Dejonghe, L. C., SOLID REDOX POLYMERIZATION ELECTRODES AND THEIR USE IN ALL-SOLID-STATE BATTERIES. *Molecular Crystals and Liquid Crystals* **1990,** *190*, 185-195.

21.   Oyama, N.; Tatsuma, T.; Sato, T.; Sotomura, T., Dimercaptan–polyaniline composite electrodes for lithium batteries with high energy density. **1995**.

22.   Oyama, N.; Pope, J. M.; Sotomura, T., Effects of adding copper (II) salt to organosulfur cathodes for rechargeable lithium batteries. *Journal of the Electrochemical Society* **1997,** *144* (4), L47-L51.

23.   Oyama, N. In *Development of polymer‑based lithium secondary battery*, Macromolecular Symposia, Wiley Online Library: 2000; pp 221-228.

24.   Park, J. E.; Kim, S.; Mihashi, S.; Hatozaki, O.; Oyama, N. In *Roles of metal nanoparticles on organosulfur‑conducting polymer composites for lithium battery with high energy density*, Macromolecular Symposia, Wiley Online Library: 2002; pp 35-40.

25.   Tatsuma, T.; Matsui, F.; Shouji, E.; Oyama, N., Reversible electron transfer reaction between polyaniline and thiol/disulfide couples. *Journal of Physical Chemistry* **1996,** *100* (33), 14016-14021.

26.   Oyama, N.; Kiya, Y.; Hatozaki, O.; Morioka, S.; Abruna, D., Dramatic acceleration of organosulfur redox behavior by poly(3,4-ethylenedioxythiophene). *Electrochemical and Solid State Letters* **2003,** *6* (12), A286-A289.

27.   Kiya, Y.; Hutchison, G. R.; Henderson, J. C.; Sarukawa, T.; Hatozaki, O.; Oyama, N.; Abruna, H. D., Elucidation of the redox behavior of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) at poly(3,4-ethylenedioxythiophene) (PEDOT)-modified electrodes and application of the DMcT-PEDOT composite cathodes to lithium/lithium ion batteries. *Langmuir* **2006,** *22* (25), 10554-10563.

28.   Tsutsumi, H.; Fujita, K., NEW-TYPE POLYAMIDES CONTAINING DISULFIDE BONDS FOR POSITIVE ACTIVE MATERIAL OF ENERGY-STORAGE BATTERIES. *Electrochimica Acta* **1995,** *40* (7), 879-882.

29.   Tsutsumi, H.; Okada, K.; Oishi, T., Electrochemical behavior of new polyamides containing disulfide bonds and pyridine rings in organic electrolyte solution. *Electrochimica Acta* **1996,** *41* (16), 2657-2659.

30.   Tsutsumi, H.; Okada, K.; Fujita, K.; Oishi, T., New type polyamides containing disulfide bonds for positive active material of lithium secondary batteries. *Journal of Power Sources* **1997,** *68* (2), 735-738.

31.   Tsutsumi, H.; Oyari, Y.; Onimura, K.; Oishi, T., Electrochemical behavior of polyamides with cyclic disulfide structure and their application to positive active material for lithium secondary battery. *Journal of Power Sources* **2001,** *92* (1-2), 228-233.

32.   Han, X.; Qing, G.; Sun, J.; Sun, T., 0-1How Many Lithium Ions Can Be Inserted onto Fused C6 Aromatic Ring Systems? *Angewandte Chemie-International Edition* **2012,** *51* (21), 5147-5151.

33.   Kaneto, K.; Yoshino, K.; Inuishi, Y., 0-2CHARACTERISTICS OF POLYTHIOPHENE BATTERY. *Japanese Journal of Applied Physics Part 2-Letters* **1983,** *22* (9), L567-L568.

34.   Kasavajjula, U.; Wang, C.; Appleby, A. J., 0-3Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells. *Journal of Power Sources* **2007,** *163* (2), 1003-1039.

35.   Shacklette, L.; Toth, J.; Murthy, N.; Baughman, R., Polyacetylene and polyphenylene as anode materials for nonaqueous secondary batteries. *Journal of the Electrochemical Society* **1985,** *132* (7), 1529-1535.

36.   Zhu, L.; Lei, A.; Cao, Y.; Ai, X.; Yang, H., An all-organic rechargeable battery using bipolar polyparaphenylene as a redox-active cathode and anode. *Chemical Communications* **2013,** *49* (6), 567-569.

37.   MacDiarmid, A.; Yang, L.; Huang, W.; Humphrey, B., Polyaniline: Electrochemistry and application to rechargeable batteries. *Synthetic Metals* **1987,** *18* (1), 393-398.

38.   Mermilliod, N.; Tanguy, J.; Petiot, F., A study of chemically synthesized polypyrrole as electrode material for battery applications. *Journal of the Electrochemical Society* **1986,** *133* (6), 1073-1079.

39.   Zhou, M.; Qian, J.; Ai, X.; Yang, H., Redox‐Active Fe (CN) 64−-Doped Conducting Polymers with Greatly Enhanced Capacity as Cathode Materials for Li‐Ion Batteries. *Advanced Materials* **2011,** *23* (42), 4913-4917.

40.   Kaneto, K.; Yoshino, K.; Inuishi, Y., Characteristics of polythiophene battery. *Japanese Journal of Applied Physics* **1983,** *22* (9A), L567.

41.   Liu, L.; Tian, F.; Wang, X.; Yang, Z.; Zhou, M.; Wang, X., Porous polythiophene as a cathode material for lithium batteries with high capacity and good cycling stability. *Reactive and Functional Polymers* **2012,** *72* (1), 45-49.

42.   Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J., Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene,(CH) x. *Journal of the Chemical Society, Chemical Communications* **1977,** (16), 578-580.

43.   Gomez-Romero, P., Hybrid organic–inorganic materials—in search of synergic activity. *Advanced Materials* **2001,** *13* (3), 163-174.

44.   Huang, Y.-H.; Goodenough, J. B., High-rate LiFePO4 lithium rechargeable battery promoted by electrochemically active polymers. *Chemistry of Materials* **2008,** *20* (23), 7237-7241.

45.   Nakahara, K.; Iwasa, S.; Satoh, M.; Morioka, Y.; Iriyama, J.; Suguro, M.; Hasegawa, E., Rechargeable batteries with organic radical cathodes. *Chemical Physics Letters* **2002,** *359* (5), 351-354.

46.   Nishide, H.; Iwasa, S.; Pu, Y.-J.; Suga, T.; Nakahara, K.; Satoh, M., Organic radical battery: nitroxide polymers as a cathode-active material. *Electrochimica acta* **2004,** *50* (2), 827-831.

47.   Nakahara, K.; Oyaizu, K.; Nishide, H., Organic Radical Battery Approaching Practical Use. *Chemistry Letters* **2011,** *40* (3), 222-227.

48.   Nakahara, K.; Iriyama, J.; Iwasa, S.; Suguro, M.; Satoh, M.; Cairns, E. J., High-rate capable organic radical cathodes for lithium rechargeable batteries. *Journal of power sources* **2007,** *165* (2), 870-873.

49.   Suga, T.; Sugita, S.; Ohshiro, H.; Oyaizu, K.; Nishide, H., p- and n-Type Bipolar Redox-Active Radical Polymer: Toward Totally Organic Polymer-Based Rechargeable Devices with Variable Configuration. *Advanced Materials* **2011,** *23* (6), 751-+.

50.   Nakahara, K.; Iwasa, S.; Satoh, M.; Morioka, Y.; Iriyama, J.; Suguro, M.; Hasegawa, E., Rechargeable batteries with organic radical cathodes. *Chemical Physics Letters* **2002,** *359* (5-6), 351-354.

51.   Suga, T.; Pu, Y.-J.; Kasatori, S.; Nishide, H., Cathode-and anode-active poly (nitroxylstyrene) s for rechargeable batteries: p-and n-type redox switching via substituent effects. *Macromolecules* **2007,** *40* (9), 3167-3173.

52.   Oyaizu, K.; Suga, T.; Yoshimura, K.; Nishide, H., Synthesis and characterization of radical-bearing polyethers as an electrode-active material for organic secondary batteries. *Macromolecules* **2008,** *41* (18), 6646-6652.

53.   Oyaizu, K.; Ando, Y.; Konishi, H.; Nishide, H., Nernstian adsorbate-like bulk layer of organic radical polymers for high-density charge storage purposes. *Journal of the American Chemical Society* **2008,** *130* (44), 14459-14461.

54.   Suga, T.; Ohshiro, H.; Sugita, S.; Oyaizu, K.; Nishide, H., Emerging N-Type Redox-Active Radical Polymer for a Totally Organic Polymer-Based Rechargeable Battery. *Advanced Materials* **2009,** *21* (16), 1627-1630.

55. Oyaizu, K.; Kawamoto, T.; Suga, T.; Nishide, H., Synthesis and charge transport properties of redox-active nitroxide polyethers with large site density. *Macromolecules* **2010,** *43* (24), 10382-10389.

56. Choi, W.; Ohtani, S.; Oyaizu, K.; Nishide, H.; Geckeler, K. E., Radical Polymer-Wrapped SWNTs at a Molecular Level: High-Rate Redox Mediation Through a Percolation Network for a Transparent Charge-Storage Material. *Advanced Materials* **2011,** *23* (38), 4440-4443.

57. Choi, W.; Ohtani, S.; Oyaizu, K.; Nishide, H.; Geckeler, K. E., Radical Polymer-Wrapped SWNTs at a Molecular Level: High-Rate Redox Mediation Through a Percolation Network for a Transparent Charge-Storage Material. *Advanced Materials* **2011,** *23* (38), 4440-+.

58. Wain, A. J.; Wildgoose, G. G.; Heald, C. G.; Jiang, L.; Jones, T. G.; Compton, R. G., Electrochemical ESR and voltammetric studies of lithium ion pairing with electrogenerated 9, 10-anthraquinone radical anions either free in acetonitrile solution or covalently bound to multiwalled carbon nanotubes. *The Journal of Physical Chemistry B* **2005,** *109* (9), 3971-3978.

59. Foos, J.; Erker, S.; Rembetsy, L., Synthesis and Characterization of Semiconductive Poly-1, 4-Dimethoxybenzene and Its Derived Polyquinone. *Journal of The Electrochemical Society* **1986,** *133* (4), 836-841.

60. Häringer, D.; Novák, P.; Haas, O.; Piro, B.; Pham, M. C., Poly (5-amino-1, 4-naphthoquinone), a Novel Lithium-Inserting Electroactive Polymer with High Specific Charge. *Journal of The Electrochemical Society* **1999,** *146* (7), 2393-2396.

61. Le Gall, T.; Reiman, K. H.; Grossel, M. C.; Owen, J. R., Poly (2, 5-dihydroxy-1, 4-benzoquinone-3, 6-methylene): a new organic polymer as positive electrode material for rechargeable lithium batteries. *Journal of power sources* **2003,** *119*, 316-320.

62. Oyama, N.; Sarukawa, T.; Mochizuki, Y.; Shimomura, T.; Yamaguchi, S., Significant effects of poly (3, 4-ethylenedioxythiophene) additive on redox responses of poly (2, 5-dihydroxy-1, 4-benzoquinone-3, 6-methylene) cathode for rechargeable Li batteries. *Journal of Power Sources* **2009,** *189* (1), 230-239.

63. Song, Z.; Zhan, H.; Zhou, Y., Anthraquinone based polymer as high performance cathode material for rechargeable lithium batteries. *Chemical Communications* **2009,** (4), 448-450.

64. Xu, W.; Read, A.; Koech, P. K.; Hu, D.; Wang, C.; Xiao, J.; Padmaperuma, A. B.; Graff, G. L.; Liu, J.; Zhang, J.-G., Factors affecting the battery performance of anthraquinone-based organic cathode materials. *Journal of Materials Chemistry* **2012,** *22* (9), 4032-4039.

65. Choi, W.; Harada, D.; Oyaizu, K.; Nishide, H., Aqueous electrochemistry of poly (vinylanthraquinone) for anode-active materials in high-density and rechargeable polymer/air batteries. *Journal of the American Chemical Society* **2011,** *133* (49), 19839-19843.

66. Nokami, T.; Matsuo, T.; Inatomi, Y.; Hojo, N.; Tsukagoshi, T.; Yoshizawa, H.; Shimizu, A.; Kuramoto, H.; Komae, K.; Tsuyama, H., Polymer-bound pyrene-4, 5, 9, 10-tetraone for fast-charge and-discharge lithium-ion batteries with high capacity. *Journal of the American Chemical Society* **2012,** *134* (48), 19694-19700.

67.   Song, Z.; Zhan, H.; Zhou, Y., Polyimides: Promising Energy‑Storage Materials. *Angewandte Chemie* **2010,** *122* (45), 8622-8626.

68.   Song, Z.; Xu, T.; Gordin, M. L.; Jiang, Y.-B.; Bae, I.-T.; Xiao, Q.; Zhan, H.; Liu, J.; Wang, D., Polymer–graphene nanocomposites as ultrafast-charge and-discharge cathodes for rechargeable lithium batteries. *Nano letters* **2012,** *12* (5), 2205-2211.

69.   Liang, Y.; Zhang, P.; Yang, S.; Tao, Z.; Chen, J., Fused Heteroaromatic Organic Compounds for High-Power Electrodes of Rechargeable Lithium Batteries. *Advanced Energy Materials* **2013,** *3* (5), 600-605.

70.   Wang, S.; Wang, L.; Zhang, K.; Zhu, Z.; Tao, Z.; Chen, J., Organic Li4C8H2O6 Nanosheets for Lithium-Ion Batteries. *Nano Letters* **2013,** *13* (9), 4404-4409.

71.   Huang, W.; Zhu, Z.; Wang, L.; Wang, S.; Li, H.; Tao, Z.; Shi, J.; Guan, L.; Chen, J., Quasi-Solid-State Rechargeable Lithium-Ion Batteries with a Calix 4 quinone Cathode and Gel Polymer Electrolyte. *Angewandte Chemie-International Edition* **2013,** *52* (35), 9162-9166.

72.   Yao, M.; Senoh, H.; Sakai, T.; Kiyobayashi, T., Redox active poly(N-vinylcarbazole) for use in rechargeable lithium batteries. *Journal of Power Sources* **2012,** *202*, 364-368.

73.   Kim, J.; Park, H.-S.; Kim, T.-H.; Kim, S. Y.; Song, H.-K., An inter-tangled network of redox-active and conducting polymers as a cathode for ultrafast rechargeable batteries. *Physical Chemistry Chemical Physics* **2014,** *16* (11), 5295-5300.

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