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An overview of feasibilities and challenge of conductive cellulose for rechargeable lithium based battery

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ABSTRACT

The interest in cellulose and its modification has been exponentially increasing. The outstanding properties of cellulose were evident due to high stiffness, high chemical resistance, low co-efficient of thermal expansion as well as high aspect ratio. Up to the present time, in order to support clean technology, the use of cellulose has been extensively gained many interests for many sectors of research. Cellulose was therefore modified to enhance its conductivity. The example was due to design cellulose based composite with conductive polymer and doping on small amount of metallic particle and active carbon. In this review, the objective of article was focused on the modification on conductivity of cellulose. The application on conductive cellulose was therefore presented in rechargeable lithium based battery.

Contents

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1. Introduction

Due to the environmental concern over the use of petroleum and petrochemical based product, this century has witnessed remarkable achievements in Green technology by means of the development on materials science to bio-based composite. Therefore, many research activities regarding bio-based materials have been extensively developed such as cellulose [1–3], chitin-chitosan [4–6], polylactic acid (PLA) [7,8], polybutylene succinate (PBS) [9] as well as natural rubber (NR) [10]. The purpose on the use of bio-based product and process was due to environmental concern. In order to support Green technology, engineering and technology should be preferably employed product and process that minimize on hazardous substance. Moreover, another aspect was involved on value-added concept. Bio-based material was considered as waste and it can be supplied as raw material for economical reason [11,12]. For example, cellulose was considered as raw material for paper-making process. Antimicrobial properties in active packaging were employed chitosan based composite. The raw material for bio-based plastic for food and beverage was involved on polylactic acid. It can be categorized into 2 different methods; the top-down approach was referred the process that biomass is subjected to high shear forces in order to create nanofibrillated cellulose [13] while the bottom-up approach was related to utilizing the biosynthesis of bacterial. The most effective bacterial specie was due to Acetobacter Xylinam [14]. From the fundamental point of view, it was important to note that cellulose was considered as the most abundant naturally occurring resource. Improvement on properties of cellulose was therefore considered as the interesting challenge for many applications. Not only availability and low cost of expenditure but also the concept of Green technology can be overcome. The role of cellulose can be employed in many applications. For example, cellulose exhibits high stiffness and high aspect ratio [15]. One of outstanding applications of cellulose was therefore encouraged as reinforcement part in composite. Mechanical properties can be consequently enhanced. If application area was related to electronic device [16–18], cellulose also present the excellence on dimensional stability [19], while if application related to food industry, it also present the excellence on water absorption ability [20]. It is remarkable to note that electronic device was generated heat during operation and food and beverage product can be highly absorbed moisture, respectively. Moreover, the role of cellulose was versatile in many engineering sectors. It included infrastructure such as building wall and bridge, automotive part such as interior and exterior console [21]. In medical and pharmaceutical research, the role of cellulose was employed; it called tissue engineering for bone repair, skin recovery technology as well as scaffold materials [22,23], whereas in electronic device, bio-based materials can offer significant feature as flexible substrate for organic light emitting diodes.

Up to the present time, the role of cellulose can be extent to electronic device society. One of interesting applications was employed as flexible substrate [16,24]. For electronic device, it was commonly fabricated by using glass sheet as substrate. Although, the use of glass sheet as substrate provides significant properties in terms of surface smoothness and dimensional stability, it offered brittleness. Currently, the use of plastic based material has been employed due to additional feature of flexibility and cost of raw materials. However, the use of plastic based electronic was limited due to low thermal resistance and low elongation at break if roll to roll (R2R) [25,26] technique was employed to fabricate electronic circuit. To overcome these limitations, it can be employed cellulose based substrate. Cellulose can be employed as flexible substrate due to excellent coefficient of thermal expansion, chemical resistance and mechanical properties [27–29].

In this review, up to the present time, numerous efforts have been extensively developed on electronic device. The development of electronic device has led to be smaller and smaller [30,31]. This evolution answers to the increasing miniaturization, high density of components with a high-reliability of device. For electronic device, lithium based battery has been widely used in many portable devices such as cell phone, laptop and camera due to the advantage of high energy density and long cycle life [32,33]. Lithium based battery was defined as disposable battery that lithium based compound was employed as an anode [34]. It stands apart from other battery due to high charge density and high cost per unit, depending on design and chemical compound. In general, it can produce voltage from 1.5 to 3.7 V [35,36]. From the viewpoint of cellulose for electronic, it was remarkable to note that cellulose has been chemically and physically modified for flexible substrate or smart paper for electronic device. To integrate with lithium base materials can be effectively performed for being developed lithium based battery on cellulose [37,38]. Many forms of lithium such as lithium-ion, lithium based oxide and lithium based conductive polymer composite has been extensively investigated for flexible feature of battery [39–41]. The incorporation of cellulose and lithium based compounds can be effectively benefited due to high flexibility, low coefficient of thermal expansion, high chemical resistance. As a result, it gained the interest on novel types of flexible battery for electronic device.

The objective of this review article was to present the state-of-art cellulose and its modification for flexible lithium based battery. Cellulose has been chemically and physically modified for its conductivity. After that, fundamental background of conductive cellulose for lithium based battery was discussed.

2. Conductive cellulose preparation

2.1. Conductive cellulose modification

In the viewpoint of energy storage device, it was important to note that significant efforts have been extremely paid attention to be researched. Due to chemical structure of cellulose which consisted of three positions of hydroxyl group, chemical modification can be therefore conducted in order to enhance the electrical conductivity of cellulose [42–45]. Due to the outstanding properties of cellulose including mechanical properties and thermal resistance, many approaches on application of cellulose was therefore developed [46,47]. Figs. 1 and 2 exhibit the structural properties and morphological properties of cellulose, respectively.

In order to realize on the importance of cellulose, this scenario was being encouraged to improve the role of cellulose in energy storage device as well as the utilization in power system. Cellulose has been extensively developed on its conductivity for 30 years ago [12,48–51]. One of attractive ways of conductive cellulose modification was considered on the incorporation with conductive polymer. In general, conductive polymer exhibits high potentiality to aggregate and ease of process-ability [51,52]. It was extremely improved and studied for many applications. One of attractive applications was involved on electro-active polymer; it effectively provided many functionalities such as dielectric and piezoelectric [53,54]. Moreover, application of conductive polymer was enrolled

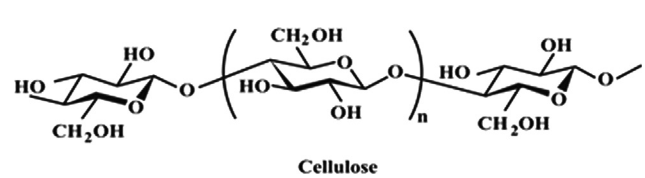

Fig. 1. Structure of cellulose.

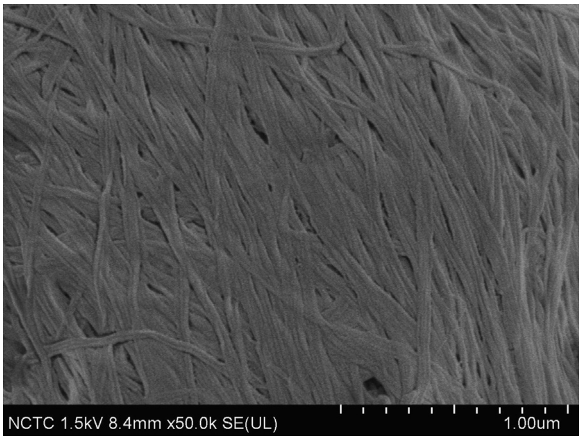

Fig. 2. Morphological properties of cellulose.

on sensor and actuator, flexible electrode as well as smart textile [55–57]. However, up to the present time, the use of conductive polymer was limited due to high thermal transition temperature, moisture sensitivity, requirement of high voltage of activation and voltage breakdown shielding. As a consequence, numerous efforts have been extensively developed on the use of conductive polymer by the incorporated into cellulose network. It can offer the thermal stability and application which required high flexibility and high vibration can be utilized. On the other hand, application of conductive cellulose was therefore versatile, conductive cellulose can be enrolled such as light emitting diode [58], field effect transistors [59] and photovoltaic cell [60,61].

Conductive cellulose, numerous efforts have extensively conducted in order to improve the conductivity and stability. One of common methods was relied on *in situ* polymerization technique [62]. The attempt was to prepare cellulose and conductive polymer as binary blend system. The example of *in situ* polymerization of cellulose and conductive polymer was successfully performed by using polyaniline (PAN) [63,64] and polypyrrole (PPy) [65,66]. In this process, *in situ* polymerization referred to a process that the monomer such as aniline and pyrrole are polymerized in the existence of cellulose and it was deposited on the surface of cellulose [67,68]. As a result, it provides continuous phase of conductive cellulose. It can be therefore prevented interface area and subsequently provided high density and toughness. Moreover, for cellulose and PPy based composite, only neat phase of PPy exhibits unstable in air due to its reactivity with a variety of atmospheric chemicals, especially oxygen. For cellulose and PPy based composite, the consideration on electrical conductivity of PPy is different and many parameters such as pyrrole concentration, oxidant charge and reaction time were therefore controlled. Moreover, it should be taken into account that modification of cellulose and PPy based composite may involve on many chemical treatments such as acid, alkaline and oxidant as well as elevated temperature which was commonly decreased on electrical conductivity.

On the other hand, in case of cellulose and polyaniline (PAN) based composite, aniline monomer was chemically *in situ* polymerization in order to form binary blend system. It was important to note that only PAN itself, it strongly employed in many applications such as diode, electrochromic, sensor as well as battery. Additionally, modification of cellulose and PAN composite can provide not only electrical conductivity, but also additional feature regarding flexibility can be enhanced. It was realized to know that cellulose and PAN based composite can be more and more employed in specific application which high vibrational force was required. Moreover, it was important to note that modification of PAN with cellulose can yield significant properties of flame retardant. Cellulose deposited with PAN yielded hollow carbonaceous microtubes after burning and this is the initiation on modification of cellulose for flame retardant by PAN insertion. Up to the present time, numerous conductive polymers have been extensively modified cellulose as composite. The example was due to poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) or PEDOT:PSS [69,70] as well as poly(allyl amine) (PAH) [71,72]. The modification on cellulose with conductive polymer as binary blend system has been extensively conducted, depending on fundamental properties of conductive polymer as well as relevant application.

From the viewpoint of material for dielectric and piezoelectric properties, the modification of cellulose with electroactive polymer was also investigated. Electro-active polymer was theoretically referred to polymer that its size and shape were changed when stimulated by an electric field [53,73,74]. The most common applications were due to sensor and actuator. A typical characteristic of electroactive polymer was due to the occurring of electric charge while sustaining large forces during the deformation of material. It was important to note that the application area of electroactive polymer was still versatile such as electromechanic sensor which small displacement was required. Moreover, in medical science area, the application related to artificial muscle, the use of electroactive polymer was evident in order to investigate on the movement of muscle by applied electric signal. The application was also extent to touch screen sensor and device.

Furthermore, investigation on conductive cellulose has been continuously developed. The conductivity level of cellulose can be enhanced by insertion of small amount metal particle or active carbon. Numerous efforts have been extensively doped metal ion as well as active carbon such as single wall carbon nanotube (SWCNT) and multiwall carbon nanotube (MWCNT) on hydroxyl position of cellulose. It was important to note that incorporation on small amount of metal particle and active carbon was involved on polarity of cellulose if it acted as island-like form [75,76]. However, for this case, percolation threshold which theoretically refereed the small amount of particle that distributed into matrix and acted as island-like structure; should be controlled. The concept was still maintained polarity in solid material without any conductive pathway among the connection among particles [77]. Up to the present time, it was important to note that only binary blend between cellulose and electroactive polymer was insufficient in order to design as electro-mechanic sensor. Any signal was insufficient in order to detect and respond. Numerous efforts have been extensively doped by incorporating the small amount of conductive particle to cellulose by chemically bonded with hydroxyl position instead of hydrogen and subsequently prepared as composite. It was remarkable that by insertion of small amount of conductive particle was beneficial; no change in morphological properties can be observed.

Another approach on conductive cellulose modification was considered on thin film formation. In this case cellulose was prepared as flexible sheet, similar to paper. Cellulose has been modified as flexible substrate for electronic device. However, this technique can be enhanced on conductivity of cellulose by deposited metallic film. In general, physical and chemical vapor depositions were extensively employed. In this technique, physical vapor deposition was theoretically referred to a variety of vacuum deposition method used to deposit thin film by condensation of a vaporized form of the desired conductive film on cellulose. This process involved physical process such as high-temperature vacuum evaporation with subsequent condensation, or plasma sputter bombardment [78,79]. While chemical vapor deposition was theoretically referred to chemical process used to produce high purity of conductive film. It involved volatile precursors that react or decompose on cellulose substrate and it resulted in conductivity of cellulose [80–82]. Although both physical and chemical vapor deposition processes can provide significant data for conductivity of cellulose, the expenditure of deposition process was still high and it should be avoided for mass production process. Also, if cellulose was considered as substrate, high water absorption ability of cellulose was still one of disadvantages for this modification.

2.2. Conductive materials for conductive cellulose preparation

In physics, conductive materials were considered as an object that permitted the flow of electrical current. Up to the present time, conductive materials were versatile and the conductivity levels depended on nature source such as conductive polymer, metallic particle and activate carbon. The role of conductive material was provided as comprehensive review as follow.

2.2.1. Conductive polymers and derivative

Conductive polymers have been discovered since two decades. Up to the present time, there are over 20 conductive polymers that have been extensively conducted on research. The example of conductive polymer was due to polypyrrole, polyaniline, polythiophene and poly(3,4-ethylenedioxythiophene), *etc.* The use of conductive polymer was still versatile, depending on application. Polypyrrole and polyaniline were commonly employed halogenated or strong polarity solvent while PEDOT:PSS was employed water as solvent. The use of conductive polymers was therefore versatile. From the fundamental point of view, the ability of conductive polymer was considered on the conduction of charge which referred to electron move within and between the polymer chains. The conductivity of polymer arised from a combination of a number of factors such as the combination between single and double bond which commonly called conjugated backbone. In conjugated backbone, single and double bonds contained a less strongly localized π bond. The p-orbital in the π bond overlap each other, allowing the electrons to be more easily delocalized and more freely between atoms.

In addition, it was important to note that to use conductive polymer with higher efficiency, effect of solvent should be remarkably considered. From the structural point of view, structure of polymer was considered as organic material and the ability of organic materials was very sensitive under solvent. Polymer solution was theoretically considered as "like dissolve like" which referred to polar polymer was dissolved in polar solvent while non-polar polymer was dissolved in non-polar solvent, suggesting that the effect of solvent should be carefully considered in order to tailor the excellent properties of conductive polymer [83,84]. This was to prevent the effect of collapse chain of polymer if non-appropriate solvent was therefore applied. In case of polymer solution, organic solvent will generate positive charge, or proton and the mobility of proton along double bond of conjugate polymer can be referred to the ability of conductivity [85,86].

In the case of cellulose and conductive polymer as binary blend system. The conductivity of cellulose can be effectively enhanced by modification as binary blend system. It was categorized as "polymer alloys". In general, the structure of cellulose was considered as network and conductive polymer part was incorporated by penetrating onto cellulose network, suggesting that appropriate polymerization should be considered on *in situ* polymerization process. It is theoretically referred to polymerization in mixture; liquid part of oligomer can be polymerized to form the solid phase and it was penetrated along cellulose network. Another aspect was due to solvent; from cellulose preparation process, the effective way to produce cellulose was based on cellulose suspension that water was employed as solvent. The use of water was preferably conducted due to environmental safety, ease of process design as well as cost effectiveness. Co-solvent by the mixture of water and alcohol based solvent such as methanol, ethanol, ethylene glycol and isopropanol was still in the experiment. Although the use of co-solvent can be offered stronger on polarity of cellulose, the significant data was still low and the process was still expensive if mass production will performed. It is inappropriate for industrial commercialization.

Another advantage on the development of conductive cellulose was due to mechanical properties. Binary blend system between cellulose and conductive polymer was not only considered on significant properties in terms of conductivity, but also the other properties including mechanical properties, thermal resistance as well as chemical resistance have been improved. However, it should be remarkably considered that interface zone between cellulose and conductive polymer part should be avoided. The use of binder should pay attention to processing process in order to prevent any failure on structure of binary blend system.

2.2.2. Metallic particle and derivatives

Metallic particle was one of alternative materials for the design for conductivity enhancement of cellulose. From the fundamental point of view, metallic particle provided strong interest due to conductivity [87,88]. Application that required high conductivity should be employed metallic particle. The example of metallic particle was due to Ag, Au and Cu particle. In electric, array of metallic particle can be employed as a pathway of electrical current. It can be passed at the interconnect between metallic particle [89,90]. The role of metallic particle can be employed in many applications of electronic device. One of attractive applications of cellulose based composite was considered on dielectric and piezoelectric properties. Due to the structure of cellulose, it was considered as network structure and there is porosity among cellulose fiber. Metallic particle can be trapped in between porosities and formed chemical bonding with hydroxyl group of cellulose. However, up to the present time, the use of metallic particle was very versatile. As a consequence, variation in size was effectively designed from micron to nano-scale. The design on metallic particle and cellulose can be enrolled on sensor technology [91], self-cleaning process [92,93] and antibacterial properties [94–96].

From the synthetic route, metallic particle was successfully prepared from two ways; the one called top-down approach which theoretically referred to breaking the solid or bulky material in order to obtain small part of metallic particle [97,98]. While the other one called bottom-up; this process was involved on the synthesis of novel material or it referred to the investigation on thermodynamic and kinetic approach. Growth of material can be prepared from both homogeneous and heterogeneous nucleations [99,100]. The advantage of top-down approach was related to cost effectiveness by milling or attrition while the advantage of bottom-up approach was due to size and geometry control. It was important to note that the role of metallic particle was versatile not only conductive feature or polar cluster material in cellulose composite but also antibacterial properties can be enhanced.

On the other hand, not only metallic particle but also metal oxide particle still exhibited strong interest for modification as conductivity or polar cluster along structure of composite. Significant efforts have been extensively developed for many types of metal oxide such as WO_3, TiO_2, ZnO as well as ZrO. From the fundamental point of view, metal oxide particle was categorized as heterostructure class of material, which referred to the interface that occurs between two layers or region of dissimilar crystalline semiconductor [101,102]. It has unequal band gaps as opposed to a homojunction. Therefore, it offered many advantages in solid state device such as semiconductor, laser, solar cell and transistors.

Due to outstanding properties of polar cluster, the combination of cellulose with metallic particle and derivatives was extensively developed in order to extend the ability of material with additional feature of flexibility to cellulose. Modification of cellulose with metallic particle and derivatives was as polar cluster was one of the most effective ways in order to modify cellulose as Electronic paper (E-paper). As a consequence, the increment on high demand to develop cellulose was therefore higher. From the viewpoint of preparation technique, many forms of metallic particle and derivatives were successfully synthesized and embedded to cellulose such as particle, tube, wire, sheet and the variation of size can be prepared from micron to nano-scale level. In general, only small amount (less than 5 wt%) of metallic particle and derivatives should be incorporated on cellulose. The investigation of the position of metallic particle was embedded on the hydroxyl position by covalently bonded with oxygen atom or by weakly bonded as van der Waal force with methyl group ($-CH_3$). It was important to note that if small amount of metallic particle and derivative was employed, suggesting that the good distribution should be considered and to prevent the agglomeration among particle should be avoided in order to obtain uniform properties to cellulose.

On the other hand, to insert the small amount of metallic particle and derivatives has been exponentially performed. It was referred to process that introduced the charge carrier (polarons and bipolarons) into cellulose and rendered its conductivity. Identically to what occur in semiconductor technology, this can occur two ways; the one was p-doping, where cellulose is oxidized and will have a positive charge. Whereas the other one was n-doping, where cellulose is reduced and will process the negative charge. Fig. 3 exhibits chemical modification of cellulose by inserted small amount of silver nanoparticle.

2.2.3. Active carbon

Up to the present time, active carbon has been extensively developed for many purposes of application. From the past, carbon was considered as char material and it was sometime considered as waste from petrochemical process [103–106]. The cost of carbon was very low. Numerous efforts have been extensively developed on both chemical and physical methods to improve the properties and value-added of carbon for many possibilities of application. One of examples in industry was focused on the use of carbon in tile and rubber industry. Modification of carbon based materials reinforced in synthetic rubber composite was very well-known for tile industry [107,108]. It was important to note that application of tile was related to thermal expansion of materials if long life cycle assessment (LCA) was operated. The objective of synthetic rubber was due to high elongation at break and flexibility, while the

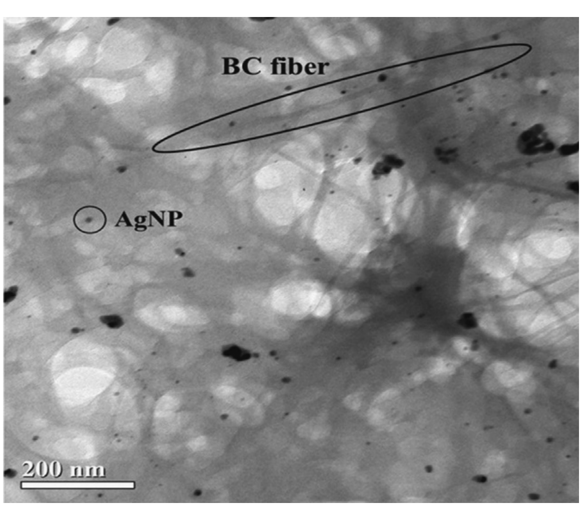

Fig. 3. Morphological properties of silver particle incorporate to cellulose.

objective of carbon material was due to thermal stability mechanical strength as well as stress transfer in between materials. Another approach was considered on carbon for bad odor elimination, it was kept in refrigerator for any sensitive gas detection, and the quality of food was maintained [109,110]. Up to the present time, numerous efforts have been conducted on modification of carbon to be active carbon. One of common methods was involved on the modification on porosity of carbon. The application of active carbon was enrolled in gas absorption sensor and wastewater treatment [111,112].

Thus far, the revolution on the development of carbon based material has been strongly evident up to the present time. Many forms of carbon can be designed such as particle, spherical shape, tube, plate as well as sheet [113–116]. This was probably due to the fact that different feature of carbon can significantly provide the difference on application. For example, carbon nanotube presented high aspect ratio and it presents the good ability if it will be applied as sensor which small detected area and displacement was applied. While, nanowire form can present the good performance on semiconductor structure and it can further be applied as dye synthesized solar cell and light emitting diode. Significant difference between nanowire and nanorod is due to high aspect ratio (L/D). Numerous efforts have been extensive designed carbon in many forms. Comparative investigation was then extent to nanofilm and nanoparticle form. The performance of surface covering by nanofilm provide significant in terms of sensitivity superior to nanoparticle. Up to the present time, the research on active carbon was also extent to carbon aerogel materials, which defined as synthetic porous carbon derived from a gel. It is ultralight weight material which composed of the liquid component of gel has been replaced by gas [117,118]. Therefore, it offered low density and low thermal conductivity. In general, the size of carbon aerogel is composed of particles with size in the nano-scale range, covalently bonded together. The range of surface area is between 400 and 1000 m^2/g and this feature was strongly evident if it can be developed as sensor material. The ability of sensor depended on specific surface area of material. In reality, the challenge on the development of carbon aerogel was related to composite preparation. Not only ability on sensor by absorption to surface but also significant enhancement on mechanical strength can be developed.

For bio-based composite, many forms of carbon were successfully developed as composite with cellulose. The role of carbon was started from gas absorption to the development of sensor ability as well as any responses [119,120]. It was important to note that the role of carbon was versatile due to controllable design on resistivity which commonly made carbon to be effective in order to design as sensor and any responses. The example of carbon for the design of composite based materials was involved on cellulose preparation. Carbon can be grafted at the hydroxyl position of cellulose and it can create the polar cluster if it will be further developed as carbon modified cellulose based composite. It was remarkably noted the covalently grafted carbon on hydroxyl group was not only provided significance on polar cluster feature but also, no change on morphological properties of cellulose can be observed.

In order to understand on the design of conductive cellulose, example of conductive material such as conductive polymer, metallic particle and active carbon is provided in Table 1

3. Structure of conductive cellulose

Up to the present time, due to the growth on industrial commercialization, the role of cellulose provided many interests in terms of engineering properties such as stiffness, toughness, chemical resistance as well as thermal resistance. It was important to note that the role of cellulose was very interesting in many

Table 1
Example of conductive polymer; metallic particle and active carbon.

Conductive polymer	Metallic particle	Active carbon
Polyfluorene	Ag	Charcoal
Polyphenylene	Au	Single wall carbon nanotube
Polypyrene	Li	Multiwall carbon nanotube
Polyazulene	Fe	Porous carbon
Polynaphthalene	Co	
Polypyrrole	Ni	
Polycarbazole	Cd	
Polyindole		
Polyaniline		
Polythiophene		

applications such as infrastructure, automotive part, electronic device as well as pharmaceutical and medical research. Prior to use cellulose in many industrial sectors, cellulose has been modified in many ways due to tailoring the excellence on correlation on conductivity, structure and cost effectiveness. However, due to the case of conductive cellulose, one way to compensate for the shortcomings of conductive cellulose is to use it together with conductive polymer, combining the positive qualities of both materials.

3.1. Binary blend

Binary blend material was theoretically referred the design on the mixture of different polymer. From the structural point of view, it was important to note that binary blend was one of effective ways to design polymer system [121]. Although only one part of polymer exhibited the strong properties, the performance of application can be effectively adjusted by incorporated with the other type of polymer. As a consequence, value-added concept can be tailored and binary blend can overcome the limitation of the use of polymer in some specific application.

For conductive cellulose, binary blend system was considered as the mixture of conductive polymer and cellulose. It was important to note that outstanding properties of cellulose were relied on stiffness, high aspect ratio as well as high thermal resistance. The role of cellulose can be employed on electronic device, the emergence on the use of cellulose has been extensively considered. It was important to note that cellulose for electronic device was strongly focused on the modification on conductivity of cellulose. In case of binary blend, cellulose and conductive polymer can be blended and offered significant properties in terms of conductivity. For example, cellulose and polyaniline (PANI) can be blended and the application of this binary blend system is focused on chemical sensor and wastewater treatment. Moreover, it was important to note that not only binary blend system with polyaniline but also polypyrrole can be blended with cellulose. The application of binary blend between cellulose and polypyrrole was focused on electronic device such as battery and supercapacitor. Binary blend system of cellulose and poly(3,4-ethylenedioxythiophene):polystyrene sulphonate (PEDOT:PSS) was successfully performed. The role of PEDOT:PSS was not only considered as conductivity but also the improvement on processing can be enhanced. It was remarkable to note that in industry, cellulose can be prepared in water based suspension form and PEDOT:PSS was also used water as solvent. The binary blend between cellulose and PEDOT:PSS was considered on the ease of processing. Both parts of material were familiar with water, suggesting that non-toxic due to solvent as well as excellent compatibility.

3.2. Doping process

Doping process was theoretically referred to adding the small amount of impurities and the property of cellulose was consecutively changed to be conductivity [122,123]. From the fundamental point of view, it was important to note that in this case, doping process was referred to the incorporation of charge carriers into cellulose and rendered its conductivity. In general, it can be observed that only small amount of impurities was introduced. The example of adding small amount of particle was due to metallic particle and active carbon. Doping process for cellulose was considered on the small amount of conductive particle to be added; the investigation on the percolation threshold on the appropriate amount of metallic particle and active carbon was evaluated. In this case, the combination between cellulose and metallic particle and active carbon was conducted and it was important to note that polar cluster of active carbon and metallic particle was formed [124]. In this case, the application was related to dielectric and piezoelectric properties of materials. The distribution of active carbon and metallic particle should be controlled in order to prevent the conductive pathway among conductive particle. On the other hand, it was remarkable to note that active carbon and metallic particle may form ionic bond with hydroxyl position of cellulose. FTIR and Raman spectroscopy can be observed about this issue [42]. By the way, the advantage of this doping is that no change can be observed on the morphological properties of cellulose.

4. Conductive cellulose for lithium based energy storage device

Up to the present time, the concern of shortage of crude oil and nuclear-based energy has extensively gained global issue. Recent development was emphasized to investigate on the novel feasibility to manage on energy based system. Many types of energy were therefore developed such as alternative energy from renewable resource. One of the most effective sources was focused on waste based energy. The reason was involved on cost effectiveness, value-added to waste, availability of raw materials Up to the present time, this challenge has been extensively gained many interests for smart city that used a stable smart grid with a clean energy power system. Clean energy based renewable energy sources and the design on clean energy storage system for electrical power supply has been widely considered an optimal solution for future smart city. In recent years, the need on energy storage device and utilization in power supplied system has long been discussed [125,126]. An overview of different storage technologies and related application has been discussed up to the present time. Fig. 4 exhibits the chemical modification of cellulose by metal ion grafting on hydroxyl position.

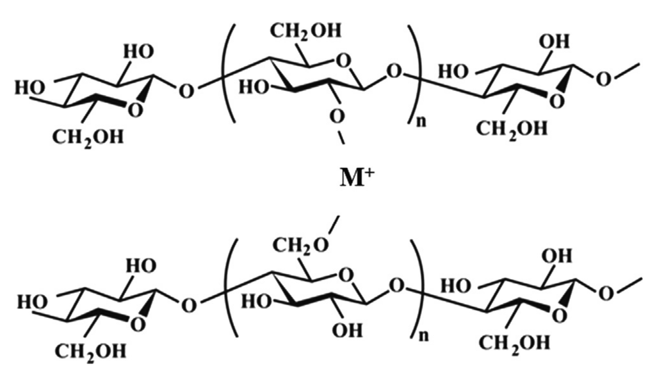

Fig. 4. Conductive cellulose network modifications.

From the past, the focus on energy storage device has been relied on lead (Pb), nickel (Ni) and cadmium (Cd) based energy storage device [127,128]. Although these energy storage devices provided significant feature in term of storage capacity, the use of these was still limited due to clean technology. From the fundamental point of view, clean technology was defined as the production of energy process, with a smaller environmental footprint and minimized pollution. Moreover, it was covered to any product or service that improved operational performance, productivity, or efficiency while reducing costs, inputs, energy consumption, waste and environmental pollution. Therefore, novel development on energy storage device has been extensively researched for sustainable and renewable energy. Up to the present time, to avoid of the use on hazardous chemicals, lithium based battery has been investigated. The role of lithium based battery was employed in consumer portable electronics due to its high energy density per weight or volume and high efficiency. However, the lithium based battery for use in stationary energy storage applications was limited owing to its high cost of lithium and it resulted on non-feasibility for mass production for industrial commercialization. In addition, lithium based energy storage device has been extensively conducted on research. The advantage of lithium based battery was due to high energy density, low self-discharge as well as low maintenance [37]. The push toward to develop lithium based battery has been therefore evident due to these reasons. From the fundamental point of view, it was important to note that lithium based battery operate by shuttling lithium ions between anode and cathode through an electrochemically insulating, ion conductive electrolyte. It is therefore interesting candidate for application that especially requires high power and energy density. Moreover, the revolution on lithium based battery exhibited the great promise as a flexible power source. Numerous efforts have been extensively developed lithium based battery with the combination of conductive polymer. The incorporation between conductive polymer and lithium based battery has been explored due to substantial advancement of flexible electronic.

In this case, for industrial commercialization, lithium based battery was considered as flexible battery. However, on the other hand, the use of cellulose was versatile and it gained many interests due to many adorable properties. It exhibited many interests for flexible electronic. The use of cellulose was satisfied on many criteria such as high aspect ratio, high stiffness, high chemical resistance as well as low coefficient of thermal expansion. It has been extremely captured many interests for modification as substrate for flexible electronic device. Due to development of lithium based cellulose materials, conductive properties have been extensively developed on cellulose as mentioned in sub topic 3. Moreover, many forms of lithium have been incorporated to cellulose [129,130]. The example of form of lithium was due to lithium-based ion and lithium based oxide ceramic such as $Li_4Ti_5O_{15}$ and $LiFePO_4$. The process related to lithium based oxide ceramic was inserted only small amount to cellulose, similar to paper making process. Small amount of lithium based oxide ceramic was incorporated in cellulose suspension and it can form the paper by filtration process. From the structural point of view, small amount of lithium based oxide ceramic can be trapped at the porous of cellulose network and offered to polarity. Another approach on conductive cellulose for lithium based battery was considered on hierarchical structure of lithium based oxide ceramic and cellulose to be formed binary blend system with conductive polymer. The example was considered on polyaniline, polypyrrole and polythiophene, respectively. It was important to note that these conductive polymers exhibited not only strong conductivity but also offered high chemical and thermal resistance. The incorporation between lithium based oxide ceramic modified cellulose and conductive polymer may offer significant properties in terms of conductivity, high thermal and chemical resistance. It is therefore appropriate if it will be employed in lithium based battery system.

To date, flexible battery has been extensively evident by many research groups. This was probably due to the next generation of technology which required flexible feature of material, convenience and ease of use. The use of lithium based oxide ceramic and conductive cellulose has been therefore developed for this purpose. There is no change on morphological properties of cellulose, while the change on conductivity of cellulose can be observed. Moreover, the environmental preservation and non-toxic material by the use of cellulose was being pushed to be investigated in many feasibilities of the use of cellulose in many engineering applications.

5. Remaining challenge

As mentioned above, the use of cellulose presented the excellence in terms of engineering properties, it was being pushed in many efforts to be developed in order to replace many engineering materials. It was important to note that the use of cellulose was interesting for environmental preservation concern. It is non-toxic and no release of hazardous compound during its both processing and application. Moreover, the properties of cellulose were evident such as high stiffness, high aspect ratio, low coefficient of thermal expansion as well as high chemical resistance. Cellulose was therefore gained more and more interest in order to develop for many purposes. Moreover, one of the challenges on the development on cellulose was due to cost effectiveness. Availability of cellulose was facile to discover. It was considered as the most abundant naturally occurring biopolymer. In this scenario, the use of cellulose was not only interested due to cost effectiveness and engineering properties, but also the concern over hazardous substance and toxic materials can be overcome. This is probably due to the reason that cellulose was being pushed in many efforts to be developed as engineering material. From the view point of flexible electronic, the role of cellulose was versatile due to interesting properties on high aspect ratio. Moreover, it will be interested if print electronic is employed to fabricate and it therefore gains many effectiveness on mass production in industrial commercialization. However, up to the present time, due to the nature of cellulose, it was important to note that the processing of cellulose was related to high amount of water, similar to paper making process. To prevent the effect of high water absorption, it was considered as one of important concerns if cellulose was employed as electronic component. In this topic, in order to use cellulose in flexible electronic for lithium based battery, it should be remarkably noted that many aspects should be carefully considered.

5.1. Long term stability

One of remaining challenges on the use of flexible electronic for lithium based battery was due to long term stability. It was important to note that although conductive cellulose was successfully designed and it satisfied the criteria on conductivity, the long term stability was still one of important aspects that have been remarkably concerned. It was important to note that in industrial commercialization, long term stability and reliability of materials should be preliminarily considered for mass production process. During operation, heat can be generated and moisture sensitivity of cellulose can be shortening the lifetime of electronic device. At this mean time, the design of conductive cellulose gained many interests due to additional feature of flexibility and conductivity.

However, the use of cellulose was still limited due to high water absorption ability that may lead to be shortening of the service lifetime of electronic device. Flexible electronic for lithium based battery should be focused on the design for no long service lifetime of material and low cost of product. However, ideally, the concept on service lifetime of material should be considered in order to extend the performance of conductive cellulose for flexible electronic.

5.2. Reproducibility

Reproducibility was considered as one of important aspects for mass production process. Prior to apply in industrial commercialization, the result from lab-scale level should be confirmed for any possibilities to be mass production process. It was important to note that the use of bio-based materials was very paid attention to be considered. Cellulose was used as raw materials and it is remarkable to understand that cellulose can be derived from plant based cellulosic materials. To use cellulose with higher efficiency, the purification on cellulose has been extensively considered. To remove lignin and hemicellulose must be carefully controlled during purification process. Moreover, the amount of cellulose that can be extracted from plant was varied due to plant species, soil condition, age of wood as well as any environmental concern. Therefore, it was remarkable to note that the raw materials for cellulose production should be consistent prior to utilization in industry. Furthermore, it is also easily to be controlled if cellulose has been furthered modified for being conductivity by means of incorporated with conductive polymer and doped with metallic particle and active carbon. In industry, the design on conductive cellulose should be well consistent due to quality control of product and process. To control properties of conductive cellulose can tentatively predicted the service lifetime of device.

5.3. Characterization the dispersion state

Characterization on the dispersion state of conductive cellulose was one of important aspects to be considered. It was important to note that the way to improve conductivity of cellulose is due to the incorporation of cellulose and conductive polymer and the insertion of small amount of metallic particle and active carbon to cellulose. Characterization on dispersion state of conductive polymer, metallic particle as well as active carbon was therefore important in order to understand the morphological properties of materials and it can be therefore used to predict mechanical properties. In this aspect, characterization of morphological properties should be carefully considered. Application involved conductivity should be concerned on the array of conductive particle while application involved dielectric and piezoelectric properties of materials should be focused on the prevention of the conductive pathway of conductive particle.

6. Conclusion and future outlook

Cellulose has been extensively conducted on research for many applications. Due to excellent properties of cellulose, it gained many interests due to high stiffness, high aspect ratio, low coefficient of thermal expansion as well as high chemical resistance. One of interests on the modification of cellulose was due to its conductivity. Cellulose was modified to be conductive by modification as composite with conductive polymer and insertion on small amount of metallic particle and active carbon. In this review, the presence on the state of art on conductive cellulose for rechargeable lithium based energy storage device has been described. The emergence on the use of conductive cellulose gained many interests due to additional feature of flexibility for portable electronic. For lithium based battery, the role of cellulose was satisfied on the design for being conductive. However, the use of cellulose was still limited due to highly absorption of water and it resulted in life cycle assessment (LCA) of cellulose in lithium based battery. To use conductive cellulose with higher efficiency, conductive cellulose was required to develop more and more on its quality and life cycle assessment (LCA) in lithium based energy storage device.

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