Nanocellulose-based polymer composites for energy applications—A review

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ABSTRACT: With rapid fossil fuel consumption and ecological concerns, alternative options of green energy development and its efficient storage technology is an emergent area of research. Nanocellulose is observed to be a very-promising sustainable and environmentally friendly nanomaterial for green and renewable electronics for advanced electrochemical energy conversion/conservation devices. This review begins with a basic introduction on the sources and properties of nanocellulose. It provides an overview of the recent advancements made by researchers in integrating nanocellulose with active materials to form a flexible film/aerogel/3D structures as a substrate for powering portable electronics, electric vehicles, *etc.* The review highlights the use of nanocellulose-based composites in energy conversion devices such as solar cells, piezoelectric materials, and lithium ion batteries. Recent research shows that the power conversion efficiency of solar cells and the piezoelectric performance of piezoelectric materials can be increased when the matrix is reinforced with nanocellulose. The review also focuses on the updates of nanocellulose-based composites in separators, binders, and electrodes of energy conservation devices such as supercapacitors, and energy capture devices such as CO_2 separators. © 2020 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2020**, *137*, 48959.

INTRODUCTION

Fossil fuel has been a major source of energy that is being used to meet the world's increasing energy demands. However, there are various negatives associated with it such as increasing pollution, global warming among others. There is an urgent need to develop devices that are energy efficient, environmentally benign, and harness energy from renewable sources.[1] The rapid advancements in technology has led to the desire to develop energy efficient conversion/conservation devices such as solar cells, rechargeable batteries, supercapacitors capable of being used in electric vehicles, aerospace and other fields. The energy efficient storage devices used today mainly include flywheels, capacitors, and superconducting magnets. These devices have some serious drawbacks such as high operation cost, high self-discharge rate, and low energy density.[2] Over the last decade, researchers have focused on making these devices affordable as well as sustainable by making use of advanced and biodegradable materials, which can be used in these energy storage devices.

Cellulose is a natural and abundant biopolymer that is being extensively used because of its attractive and tailorable physical,

chemical, and barrier properties. Cellulose, also known as cellobiose, is a high-molecular-weight homopolymer of β-1,4-linked anhydro-D-glucose units. Intermolecular and intramolecular hydrogen bonding is present between the glucose units mainly due to the presence of hydroxyl groups in it. Cellulose (35 to 50% by dry weight) obtained from trees is present in the cell walls along with other major components such as lignin (10 to 25% by dry weight) and hemicellulose (20 to 35% by dry weight) in the form of fibers.[3] The bundle of fibers is broken down mechanically and treated chemically to get rid of the unwanted components namely lignin and hemicellulose. Nanocellulose (NC) is a type of cellulose, which has one of its dimensions in the nanometer range (<100 nm). It is chiefly classified into cellulose nanocrystals (CNCs), cellulose nanofibers (CNFs), and bacterial cellulose (BC) (see Table I). It can be obtained from numerous sources such as trees, shrubs, herbs, algae (Cladophora), bacteria (Gluconacetobacter, Acetobacter, Azotobacter), and even some animals (Tunicata).[4] CNFs consists of both amorphous and crystalline regions. The amorphous regions are removed using controlled hydrolysis thus giving rise to highly crystalline CNCs. CNCs possess a large surface area and has a

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large number of surface hydroxyl groups. CNFs, on the other hand, are produced through a series of processes namely purification and fibrillation. Non-cellulose components are removed during the purification process, while mechanical fibrillation is carried out to destroy the intermolecular attraction, which enables separation of CNFs from the raw materials.[5–7] Bacterial cellulose is obtained from low-molecular-weight carbon sources through a series of biotechnological processes. Various factors such as bacterial strains, conditions, and post processing can be controlled to obtain desired nanofiber structure. Bacterial cellulose can also be used to produce CNCs.

In the recent years, researchers have focused their attention on developing NC and NC-based composites as NC is abundant, renewable, biodegradable, and ecofriendly.[10] Numerous methods such as solvent casting, melt mixing, *in situ* polymerization, extrusion and layer by layer formation have been used to prepare

Table I. Family of NC: Sources, Extraction, Dimensions and Properties

Type of cellulose	Sources	Extraction process	Dimensions	Properties	References
Cellulose Nanocrystals (CNC)	Bark of mulberry, tunicin, cotton and wood.	Acid Hydrolysis	100 nm < l < 250 nm	High crystallinity	Reference 8,9
			5 nm < d < 70 nm	Shorter Length	
			Discrete rod -shaped particles	Low aspect ratio	
Cellulose Nanofibers (CNF)	High plants such as sugar beet and potato	Mechanical processes	l = several mm	Low crystallinity	Reference 8,9
			5 nm < d < 60 nm	Longer Length	
			Network structured nano-scaled fibers	High aspect ratio	
Bacterial nanocellulose (BC)	Gram negative bacteria	Bacterial synthesis	20 nm < d < 100 nm	High aspect ratio	Reference 4,8,9

NC-based composites.[11] NC has attractive mechanical properties such as high tensile strength (14 ± 8 GPa),[12] tensile modulus of approximately (100 ± 40 GPa),[5,13,14] stiffness and low density (1.5 ± 0.1 g/cc),[15] which led to its use as reinforcing agent in polymers. It also possesses other excellent properties such as flexibility, transparency, and low thermal expansion, which has made it a potential candidate for various applications.[16,17] NCs are also found to have unique dielectric properties enabling their use as insulating material. However, this dielectric property is significantly impacted by the presence of moisture.[18] NC has found extensive applications in various domains such as medical and pharmaceutical, food packaging, water filtration, membranes, sensors, solar panels, capacitors, paints, and coatings.[19–22] However, there are certain disadvantages associated with it such as high moisture absorption and formation of agglomerates, which has hindered its widespread use.[23]

Numerical Studies—As the mechanical properties of NC and hence its composites vary based on its source (aspect ratio) and the processing of it, it is important here to mention the efforts taken by the researchers who carried out numerical investigation highlighting the importance of these variables on the properties of the resultant nanocomposites. For the simulation of nanocellulose, Lopez et al. employed MARTINI coarse-grained model using force filed parameters.[24] This model was not only able to reproduce different properties of cellulose Iβ but also visualize the physical response of it to thermo-mechanical stimuli. Sapkota et al. described a model to estimate the mechanical properties of the polymer composites containing binary nanofillers having different aspect ratios.[25] They were able to explain the dominance of the nanofiller having higher aspect ratio on deciding the resultant properties of the nanocomposites. A network forms when the concentration of the nanofiller reaches a critical value termed as the percolation threshold. This model was also able to predict the percolation threshold for nanocomposites employing two different nanofillers having different aspect ratios. Gooneie et al. utilized dissipative particle dynamics method and observed the effect of aspect ratio on nanofiller dispersions in polymers.[26] They correlated the nanofiller length and kinetics of their self-assembly in polymer composites. The equilibrium morphology simulations were in good agreement with the experimental ones and was concluded that the long nanorods could self-assemble into ordered honeycomb-like bundles. Rojas et al. also carried out dissipative particle dynamic simulations to determine if the corona of grafted polymer molecules as well as the polymer mediated interactions between the grafted particles inherits the polygonal character of the cross-section of CNC aggregates.[27]

Over the past few years, researchers have published various papers based on the incorporation of NC and NC-based composites in energy conversion and conservation devices.[28–30] Apart from displaying high cell capacitance, efficient charge-discharge rate and good cyclic performance, NC-based nanocomposites also possess piezoelectric properties, which can be exploited through their incorporation in energy-based devices.[31] CNCs also possess excellent mechanical properties and high moisture uptake ability, which makes them suitable candidates to be used as alternatives in membranes of energy conversion devices such as CO_2 separators.[32] This review elaborates on aspects such as improving the power conversion efficiency (PCE) of solar cells, finding alternatives to traditionally available piezo-electric films, replacing petroleum-based material by NC-based materials in energy storage devices such as supercapacitors and lithium ion batteries. It also has discussed the challenges that need to overcome before such environmentally benign composites can be commercialized.

NANOCELLULOSE IN ENERGY CONVERSION DEVICES

Nanocellulose-Based Composites for Solar Energy Applications
A range of materials (Silicon and group III–V elements) have been used in solar cells to efficiently convert solar energy. Inorganic materials when used in solar cells have shown a PCE ranging between 10 and 30%, while organic materials have a PCE of around 2.5%.[33] However, the cost of manufacturing solar cells using inorganic materials is very high. The use of biomaterials in solar cells is currently being explored as they are sustainable, renewable, and abundant in nature. In order to efficiently convert solar energy into electric energy, it is vital that the conversion devices have a large surface area and good charge transport properties. CNCs have a high optical haze making them highly suitable to be used in high efficiency conversion devices.[34] Zhou et al. made significant contributions in developing recyclable solar cells using CNC and silver to develop a semitransparent electrode recyclable solar cell. These solar cells were found to have a conversion efficiency of 2.7%.[35] They further developed solar cells with CNC as a substrate using film transfer lamination and found the conversion efficiency to be 4%.[36]

Organic photovoltaic devices—Organic photovoltaic devices mainly make use of materials such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) as substrates. Costa et al. made use of glass, CNC, and CNF films as substrates in organic photovoltaic cells and obtained PCE of 3, 1.4, and 0.5%, respectively.[37] Cells using CNC films as a substrate were found to have higher efficiency as compared to cells using CNF as the CNC films were smoother, distribution of fibers was more homogenous and roughness was low. Papers developed from CNCs can also be used in photoactive components of solar cells as substrates and electrolytes as they can be made transparent by various methods such as TEMPO oxidation where a transparency of up to 90% can be obtained and can scatter light in the direction of transportation. The above effect is mainly observed as the dimensions of CNC are much less than the wavelength of light. These papers have better photon absorption rates when ambient light is incident at oblique angles and have a potential to replace glass substrates.[38,39] Nge et al. developed a nano fiber paper using Ag nanowires and CNF's, which was then used as a substrate in organic solar cells. The resistance of the paper was found to be constant after 20 folding cycles. These solar cells reported a PCE of 3.2%.[40] Cheng et al. developed O-(2,3-Dihydroxypropyl) Cellulose (DHPC)-based nano papers, which exhibited high levels of transparency but low mechanical properties.[28] In order to reinforce the papers, tunicate cellulose nanocrystals (TCNCs) having a high aspect ratio of 72 were added to DHPC. This led to the formation of percolating networks and enabled stress transfer in the composite material. The material was coated with tin-doped indium oxide without glue to form an electrode and reported a PCE of 4.98%. Chen et al. developed superhydrophobic cellulose
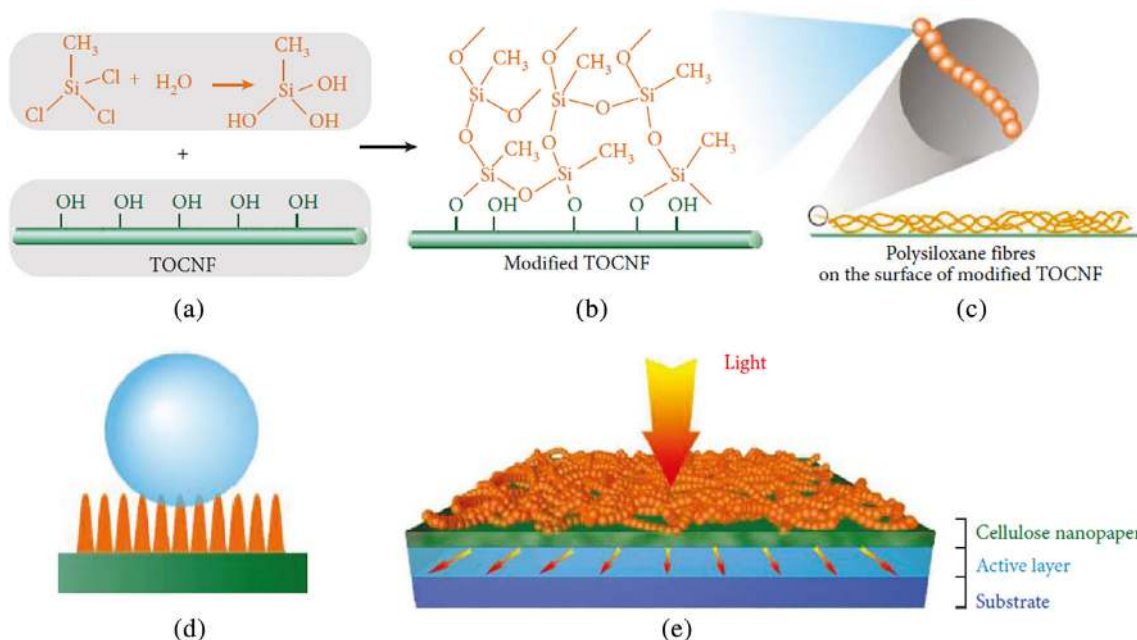
Figure 1. (a), (b), (c) CNP with TEMPO oxidized CNF (d) The CNP is made superhydrophobic due to the presence of polysiloxane (e) High haze presented by the CNP optimizes its performance. Reproduced with permission.[41] [Color figure can be viewed at wileyonlinelibrary.com]

nano papers (CNP), which had polysiloxanes polymerized onto its surface as shown in Figure 1.[41] The cellulose nano papers, which were mainly comprised TEMPO-oxidized CNF were reported to have high transparency and haze and a static water contact angle of 159.6[0]. Due to the super hydrophobic nature exhibited by this CNP, dust and water could not stick onto the surface of the solar cell, which thus enhanced the performance by 14% as compared to a bare cell and the PCE was reported to be as high as 11.48%.

Perovskite solar cells—Perovskite solar cells (PSCs) have a low cost and a high energy conversion efficiency and have the potential to be used in wearable electronics. It is observed that the PCE of Metal hydride perovskite cells (23.3%) is very close to the crystalline silicon cells (26%). PSCs are usually fabricated using petroleum-based polymer substrates, which are a major source of pollution. However, Gao *et al*. fabricated these PSCs using acrylic-coated NC papers as a substrate, which are ecofriendly and less polluting. The PSCs were found to have a power to weight ratio of 0.56 W/g, energy conversion efficiency of 4.25%,

and were capable of retaining more than 80% of their efficiency even after undergoing bending 50 times.[42] Gao *et al*. attempted to replace the traditional silicon-based solar energy conversion devices with perovskite solar cells (PSCs). Recently, Yang *et al*. fabricated perovskite films with an enlarged grain size and decreased defect density by introducing a low cost green polymer, ethyl cellulose into the layer.[43] The resulting device has shown the PCE to 19.27% and hysteresis index decreased by three times. As seen in Figure 2, the device when compared without ethyl cellulose, has displayed long-term environmental stability.

Dye Sensitized Solar Cells—Jomar *et al*. made use of raw cellulose and cellulose nanocrystals as a precursor for carbon nano dots, which was used as a photosensitizer in dye sensitized solar cells (DSSC). A larger yield of carbon nano dots was obtained with CNC (54.6%) as compared to raw cellulose (37.2%).[44] Bella *et al*. developed DSSC with an aim to replace petroleum-derived polymeric matrices with green jellifying agents such as carboxymethylcellulose (CMC) and overcome the problem of moisture/
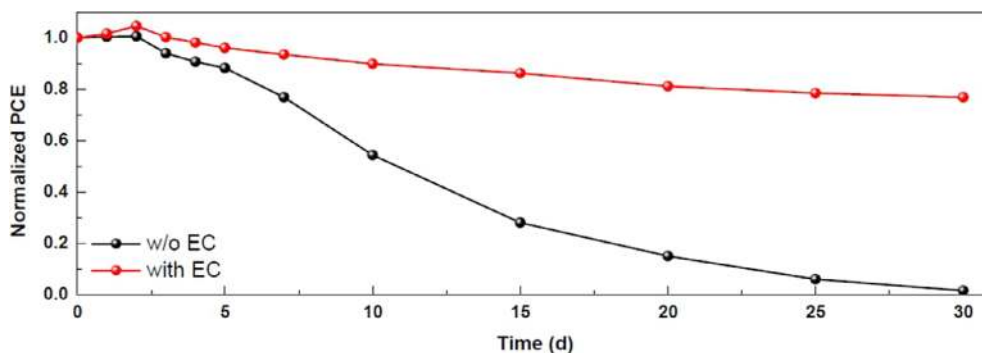

Figure 2. A comparison on the basis of stability of bare perovskite solar cells with and without Ethyl Cellulose. Reproduced with permission.[43] [Color figure can be viewed at wileyonlinelibrary.com]
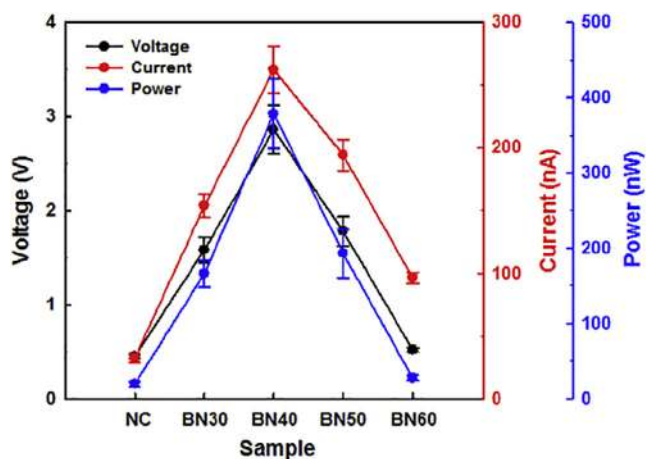
Figure 3. A plot of the output piezoelectric voltage, current, and power of a nanocellulose composite film as the concentration of BaTiO3 is changed under a periodical compression stress of 5 kPa. Reproduced with permission.[31] [Color figure can be viewed at wileyonlinelibrary.com]

water contamination in solar cells. The DSSC's reported a photovoltaic performance of 0.72% when 5.5 wt.% CMC was used as an electrolyte and good stability even under aging conditions.[45]

Many obstacles have yet to be surpassed before NC can be used for mass production of solar devices. One of the major challenges researchers face is developing cost effective as well as time intensive methods for the extraction of nano cellulose and their fabrication into solar devices. Improving the shelf life as well as stability of nano cellulose-based solar devices under humid conditions is another aspect, which researchers need to investigate.

Nanocellulose-Based Composites for Piezo-Electric Application
Piezo electricity is the development of electric charges in crystalline materials due to mechanical stimuli such as compression, tension, bending, twisting. Piezo electric films made up of polyvinylidene difluoride are commercially being used.[46] The commercially available flexible piezoelectric films are made up of Polyvinylidene Fluoride (PVDF). These films are expensive and nonbiodegradable. A new trend of incorporating nanocellulose in composite films has been observed. Hanninen et al. fabricated a CNF and chitosan-based green piezoelectric material using solvent casting method and measured their piezoelectric response.[46] Plain chitosan film displayed twice the higher piezoelectric sensitivity (5 pC/N) than the quartz crystal (2 pC/N), demonstrating it as a candidate for biodegradable, sensor material. The blend of chitosan-CNF showed lesser sensitivity (2 pC/N) than the plain films of chitosan and CNF (8 pC/N). A similar piezo electric film was developed using microcrystalline chitosan and nanocellulose and the piezo electric response was found to vary between 2 and 8 pC/N.[46] Csoka et al. developed ultrathin films, which had CNC's arranged in different degrees of alignment. A higher piezo electric effect was observed by the author for films having higher degree of alignment.[47] Csoka et al. also developed similar CNC films having highly ordered crystal structures and obtained a piezoelectric constant (d_{25} = 2.1 Å/V) through atomic force microscopy measurements.[48] Choi et al. fabricated nanocellulose-

barium titanate composite film by aqueous suspension casting followed by electric poling.[31] They studied its piezoelectric performance as a function of $BaTiO_3$ content and found high piezoelectric performance at 40 wt% (Figure 3). This 30-μm film showed excellent piezoelectric performance (2.86 V, 262.4 nA current, 378.2 nW power under a low compressional stress of 5 kPa) at par with their PVDF-BaTiO$_3$ composite counterparts.[49,50] The sensor characteristics of the self-standing CNF film was compared with PVDF piezoelectric polymer.[51] The sensor sensitivity of CNF film (7pC/N) was found to be four times lesser than the PVDF film (27.5 pC/N). But linearity between force and sensor charge and spontaneous polarization under applied stress revealed that the CNF is a candidate as a piezoelectric material for disposable piezoelectric sensors and actuators. Comparatively, regenerated CNC has high apparent piezoelectric coefficient ranging 35–60 pC/N.[52]

To increase the piezoelectric charge constant (increased to 93.5 pC/N), cellulose film was coated with ZnO nanolayer by spin-coating method.[53] To make it suitable for mass production, Ko et al. proposed hydrothermal synthesis method.[30] Fabrication by twice hydrothermal reaction displayed 1.6 times piezoelectric charge constant (37.4 pC/N) compared with single hydrothermal reaction (23.4 pC/N); still approximately one third of the spin-coated ones. A method should be developed that can assist in orientation of the CNCs in the film. A proper orientation will improve the tensile properties and piezoelectric sensitivities. Another concern is related with the brittleness of the biopolymers. Brittleness can be reduced with the addition of plasticizers to it. But its effect on piezoelectric sensitivity is required to be studied.
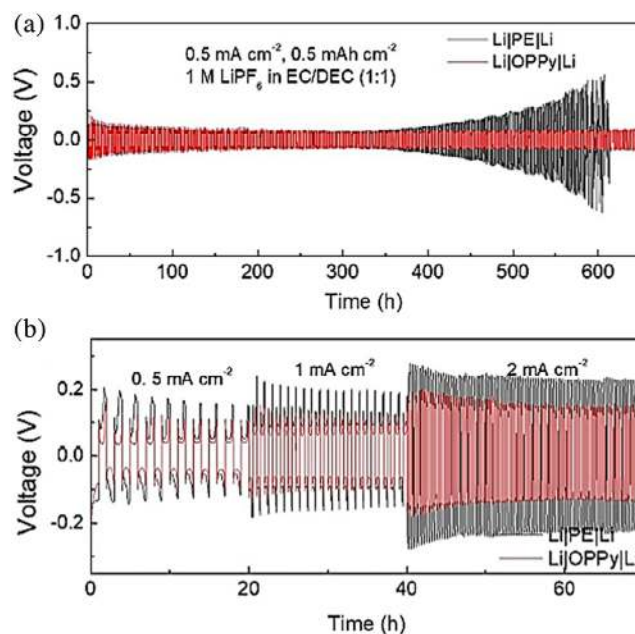

Figure 4. (a) Voltage versus Time plot of Lithium cells with PE and OPPy separator at a current density of 0.5 mA/cm^2 and fixed oxidation/reduction charge of 0.5 mAh/cm^2 (b) Voltage versus Time plot with varying current densities. Reproduced with permission.[63] [Color figure can be viewed at wileyonlinelibrary.com]

Nanocellulose-Based Composites for Lithium Ion Batteries

Lithium ion batteries (LIBs) are important energy storage devices that have found wide application in cars, cameras, mobile phones, power sources, and so forth. They are attractive mainly because of their low self-discharge rate, high cycle life, energy density, and performance. Traditionally graphite has been used in these batteries as an anode electrode mainly because of its high electrical conductivity ($\sim 10^3$ S/m) and theoretical capacity (372 mAh g^{-1}). A major drawback of graphite-based electrodes is that they do not possess sufficient energy density required to meet today's energy demand and have higher cost. Nowadays there has been a growing focus on the use of nanomaterials in such flexible energy storage devices.[54,55]

Separators—LIBs mainly consist of an anode, cathode, electrolyte, and a separator membrane. Polyethylene (PE) and polypropylene (PP) are mainly being used to manufacture this separator membrane due to their excellent chemical stability and high mechanical strength.[56] Surface modification of these separator membranes with organic (polyethylene oxide) and inorganic materials (Al_2O_3) has become essential to overcome the poor electrolyte wettability and low thermal stability of the unmodified membranes.[57,58] However, this may lead to blocking of pores, which reduces the amount of Li$^+$ ions passing through the separator.[59,60] Advanced research in this field has shown that NC can be used as a potential performance improver in the form of a membrane enhancer or a membrane gelator as it possesses properties such as excellent electrolyte wettability and high thermal stability.[61,62] Wang et al. manufactured Over oxidized Polypyrrole (O-PPy) paper from PPy-NC composite and employed it as a separator.[63] It was observed that the cell containing this separator exhibited a longer cycle life and could be cycled for more than 600 h [Figure 4(a)] as the required Li morphology could be obtained using O-PPy separator. Voltage hysteresis effects were also observed to be lesser compared with the cell containing PE separator. Pan et al. fabricated a sandwich structured separator containing two outer layers of CNF with a layer of glass microfiber sandwiched in it.[64] The objective was to create a homogeneous distribution of nanopores in the outer CNF layers to attain balanced current distribution at both electrodes and macropores at the intermediate glass layer to facilitate the ionic transport through the separator. It was also observed that the separator pore structure (high porosity and its homogeneous surface pore distribution) improved the capacity and stability of Lithium metal batteries substantially. A functionalized separator containing insulating layer of NC and polydopamine/carbon nanotubes (CNT) redox active layer was manufactured using a facile paper manufacturing process by Pan et al.[65] Due to additional capacity provided by the redox-active layer, the capacity of LIB was increased when replaced it with conventional separator without increasing the size of the cell. This led to an increase in energy and power densities of LIB.

Lalia et al. showed that CNC can be used as a reinforcing agent in Polyvinylidene fluoridehexa-fluoropropylene-based membranes.[66] As CNC is soluble in water it can be a potential replacement to the perilous organic solvents typically used in these batteries.[67]

Electrodes—Wang et al. developed a CNC/carbon nano tube (CNT) and Si-based anode and found its specific capacity to be in the range of 800 mAh g^{-1}.[68] Carbonized CNC electrodes on the other hand were found to have a 94.8% capacity retention after 300 cycles thus indicating long cycle life.[55] Kim et al. developed Lithium metal batteries having Lithium iron phosphate (LFP) as a cathode and Lithium metal as an anode.[55] When a coating of carbonized CNC (c-CNC) was applied on the PP membrane, the initial discharge capacity of the cell was found to be 136.08 mAh/g as compared to 130.2 mAh/g without coating on the membrane (Figure 5). The authors stated that the cell with a coating of c-CNC had higher electrical conductivity as they showed the smallest polarization gap. The discharge capacity was found to fall to 114.7 mAh/g for the cell with a coating of c-CNC after 500 cycles and 109.6 mAh/g for the cell without coating.

NANOCELLULOSE IN ENERGY CONSERVATION DEVICES

Nanocellulose-Based Composites for Supercapacitors

Supercapacitors have been identified as future prospects to be used as energy storage devices mainly because of their high shelf life, high power and energy density, larger range of operating temperatures, long cycle life, rapid charge/discharge rates, low maintenance cost, etc.[69] Based on charging-discharging mechanism, supercapacitors are classified as electrochemical double layer cCapacitors (EDLCs) and pseudo capacitors. The capacitive performance of the EDLCs depend upon the conductivity and the surface area of the electrode. Higher is the surface area, higher will be the ions adsorbed at the interface and hence higher will be the energy storage. Whereas, the rate of (reversible) redox reaction between the functional groups of electrode and electrolyte, and the conductivity of the electrode determine the capacitive performance of the pseudocapacitors.[70–72] In short, the power density of EDLCs is higher whereas pseudo capacitors demonstrate higher energy density. The concept of hybrid supercapacitors combines the advantages of both and hence are preferred over batteries (high energy density) and capacitors (high power density).

NC has high strength, modulus, and aspect ratio. It is stable in most of the solvents and the stability has wide electrochemical window. Hence it can be used as a separator, electrolyte, or binder material also. As it contains highly reactive —OH groups at surfaces, it is easy to chemically modify the surface and the properties of the resultant nanocomposite can be adjusted to improve the electrochemical performance for a given application.[73,74] As CNC has a high surface area as compared to CNF/BC, they have a large number of active sites making them a suitable candidate to be used as electrodes.[75] A separator requires high mechanical strength and flexibility along with good dimensional, thermal and chemical stability. It must have high porosity to retain electrolyte in it. The nanoorder scale of NC offers a very high surface area that assists in controlling the pore structure in separators. It offers a perfect diffusion path for an electrolytic solution and facilitates the transport of ions. If used as an electrode, NC provides mechanical strength and flexibility to such electrodes (films or aerogels) and offers very high surface area that improves its capacitive performance. Conductivity of such an electrode can be increased by loading it with conductive carbonaceous materials like CNTs, graphene oxides (GO).[76,77]

2D Supercapacitors—A 2D flexible supercapacitor is attractive and useful in portable and wearable electronics. 2D paper supercapacitor was prepared by directly coating CNT ink on A4-sized cellulose paper. Mechanical strength and stability of the paper was found better compared to normal paper. It demonstrated higher capacitance compared with when PET was used as a substrate. In a similar way, flexible supercapacitors can be prepared by printing, filtration, or coating methods employing various either carbonaceous materials, conductive polymers or metal oxides.[78–80] Among these processing methods, conformal coating offers higher strength, flexibility, and mass loading as well. The conformally-coated pyrrole on cationic NC has displayed high normalized volumetric (122F/cm^3) and gravimetric (127 F/g) capacitances at 300 mA/cm$^{2.72}$ Zhang *et al.* fabricated paper-based flexible supercapacitor containing NC and CNTs and observed higher mechanical strength over traditional supercapacitors.[76] Many researchers have also proposed the preparation of electrodes in the form of films of graphene and NC. Such supercapacitors wherein both have a high specific surface area, exhibit high mechanical strength, fast charge–discharge, high cyclic stability, and high power density (1749 mW/g).[1,77,81,82] In order to test the cycle life of the electrode, 1.6 A/g current density was passed through an electrode composed of cellulose-based aniline, graphene, and silver. A 108% power density, 98% energy density, and 84% capacitance was retained after 2400 cycles, thus highlighting the mechanical stability and high cycle life of the electrodes.[83]

Electrodes—Polypyrrole (PPy) was used along with CNC to develop highly porous nanocomposite electrodes through a process of electrochemical codeposition. The electrodes were found to have a capacitance of 336 F/g and a superior stability (ability to retain 70% of its capacitance after 10 000 cycles and 47% of initial capacitance after 50 000 cycles), which is significantly greater when compared to electrodes made using PPy doped with Cl$^-$ having a capacitance of 258 F/g.[84,85] NC/conductive polymer composite has less conductivity (up to 8 S/cm). Such composites have a capacitance of 248 F/g and the ability to retain 90% of its capacitance at 0.1 V/s.[86] A similar superior capacitance of 488 and 69 F/g was observed when CNC was used along with polyaniline and poly(3,4-ethylenedioxythiophene) in electrodes as compared to 358 and 58 F/g in the absence of CNC, respectively.[87] To address this conductivity issue, ternary composites of conductive polymer/NC were fabricated where the third phase was mostly graphene or graphite.[88] Electrochemical performance of electrodes can also be improved by incorporating either metal oxide or metal hydroxide to NC-based composites.[89,90] When electrodes made of GO, PPy, and cellulose paper substrate were tested, a capacitance of 1.2 F/cm^2 at 2 mA/cm^2 was obtained and the retained permittivity after 5000 cycles was found to be 89%.[1,82]

Aerogels—NC-based aerogels are highly porous, have very low density, and large surface area and hence preferred as substrates.[91,92] CNC-based aerogels when used along with active nanoparticles such as those of manganese dioxide and PPy-coated CNTs, were able to
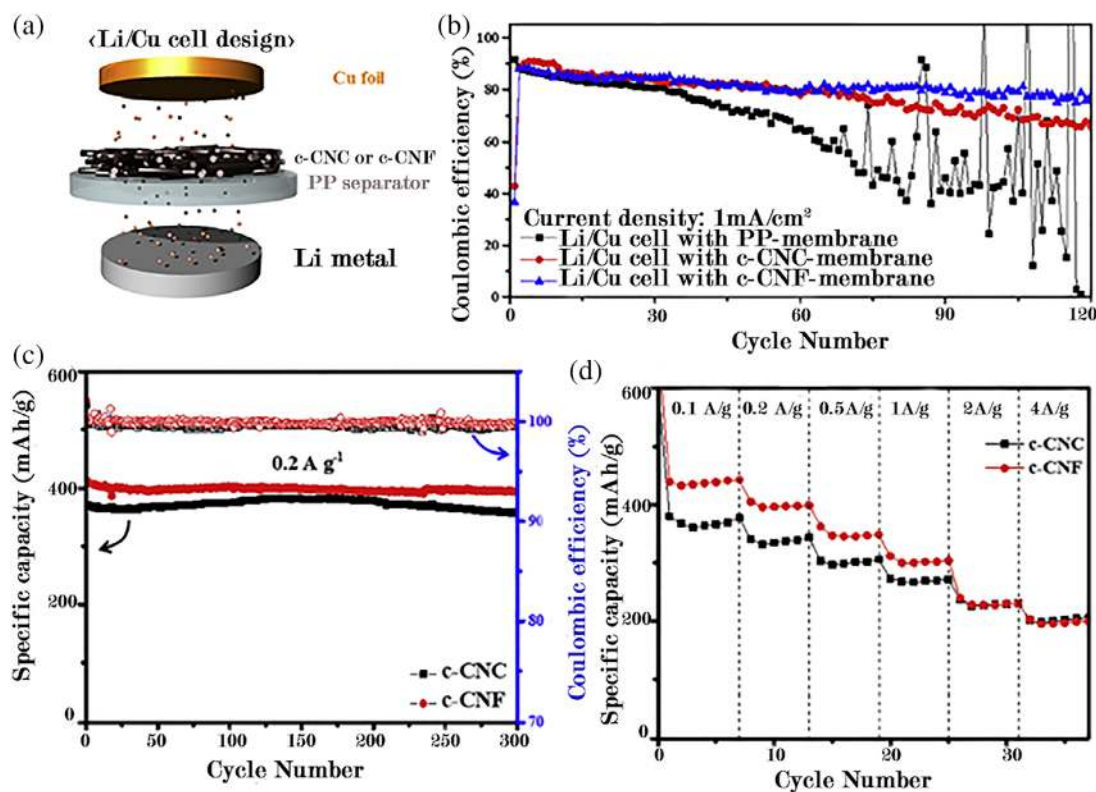

Figure 5. (a) Cell configuration of a Li/Cu cell; (b) Cyclic performance of a Li/Cu cell, (c), (d) cyclic performances and rate test. Reproduced with permission.[55] [Color figure can be viewed at wileyonlinelibrary.com]

store a significant amount of charge mainly due to the presence of a large number of active sites.[75] Electrodes prepared from aerogels comprising cellulose, reduced graphene oxide, and CNTs were found to have a capacitance of 252 F/g when the current density was 0.5 A/g. At 1 A/g, the capacitance was found to be 99% that of the initial value after 1000 cycles.[93] Wei et al. fabricated CNF-based aerogels that can retain its shape in water as well due to hydrogen bond formed between them.[94] Comparative Electrochemical performances of different NC-based polymer nanocomposites are shown in Table II.

3D Supercapacitors—Energy density can be improved further by making 3D energy storage devices. Three-dimensional cellulose-graphene structures were prepared through *in situ* polymerization and used in supercapacitors. It was noted that after 2000 cycles, the capacitance was 90.3% of its original value, which was found to be 160 F/g at a current density of 0.4A/g.[95] Liu et al. prepared a 3D scaffold of NC/GO that observed higher conductivity.[77] The bond between hydroxyl group of NC and carboxyl group of GO has not allowed the stacking of GO layers and has also prevented the aggregation of NCs in the scaffold. Similar three-dimensional structures of NC-graphene-PPy were also prepared. The composite was found to retain 93.5% of its initial capacitance (556 F/g) after 2000 cycles.[77,95] Wu et al. made a three dimensional scaffold by increasing the thickness of the aerogel with increased surface area and porosity.[96] Apart from aerogels, wood-based materials have also been emerged as 3D electrodes for energy storage devices. With wood-based 3D electrodes, it is possible to increase thickness and mass loading of the electrodes as well.[97–100] It offers an advantage of low tortuosity and straight channels that speeds up the ion transport. Manufacturing of such wood-based 3D electrodes follow top-down approach wherein the characteristic features of wood (ie. Multiple channels aligned altogether) can be retained. Wood can also be carbonized to collect current and electrode active material (lithium ion phosphate, sulfur, sodium metal, *etc.*) can be infiltrated into the pores. Chen *et al.* prepared 800-μm thick 3D wood carbon cathode and infiltrated lithium ion phosphate slurry into the channels as shown in Figure 6(a).[99] Mechanical stability and cyclic performance of such a 3D electrode was observed superior than the ones that were manufactured using slurry coating method [Figure 6(b)]. Carbonized wood is still less sturdy compared with Al or Cu foil current collectors. Other limitation is the scalability, which is maximum up to the size of the wood slice itself.

CNC in the form of porous carbon has also been used to develop chiral nematic mesoporous carbon, which when used with H_2SO_4 as an electrolyte show capacitance in the range of 170 F/g at a current density of 230 A/g.[101,102] Porous carbon materials have also been developed using CNF and CNC, which are compatible in supercapacitors. These materials when used as electrodes are found to support rapid movement of ions and are found to have a capacitance of 170 F/g.[103] Carbonized NC and the derivatives of cellulose can also be exploited in making supercapacitors.

The preparation technology in making big-sized electrodes/supercapacitors (that too with large scale production) is also a challenge to overcome. Secondly, the pore size and its distribution in NC affect the electrolyte uptake, ionic conductivity, and hence the performance of supercapacitor. It is very much required to control these parameters and prevent the collapse of the web

Table II. Comparison of Electrochemical Performance of Supercapacitors

| Composite material	Capacitance (F/g)	Capacitance retained	Current density (A/ g)	Number of cycles (cycles)	References
Cellulose based aniline, graphene and silver	-	84%	1.6	2400	83
Aerogels comprising of cellulose RGO and CNT used as electrode	252 (at 0.5 A/g)	99.5%	1	1000	93
PPy/ CNC	336	70% 47%	-	10 000 50 000	84,85
Three-dimensional cellulose-graphene structures	160	90.3%	0.4	2000	77,95
Three-dimensional structures of NC/graphene/PPy	-	93.5%	0.4	2000	77,95
CNC/PPy/polyvinylpyrrolidone (PVP)	322.6	91% 87%		1000 2000	75
Melamine-formaldehyde (MF) coated CNCs	352 (at 5 A/ g)	95.4%	20	2000	104
Carbonized CNC		94.8%	0.2	300	55
CNF/ CNT/ RGO as electrode	252	99.5%	-	1000	93
CNF/GO/PPy as electrode	334	100%	-	2000	105
CNF's/ GO as electrode	300	95.4%	-	3000	106
BC/ GO as electrode	160	90.3%	-	2000	77
PEDOT-PSS (poly(3,4-ethylenedioxyiophene)-poly(styrenesulfonate))/ SnO$_2$/ RGO/ BC as flexible electrodes	-	84.1%	2	2500	107
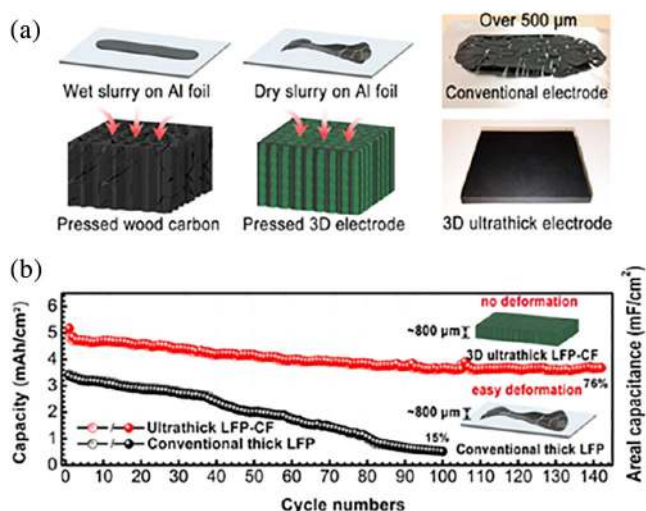
Figure 6. (a) Comparison of deformability between a conventional electrode and a 3D wood carbon electrode (b) Cyclic performance of both electrodes. Reproduced with permission.[99] [Color figure can be viewed at wileyonlinelibrary.com]

structure of NC for improved performance in energy storage systems. To impart flexibility to the electronic storage systems, the processing route to be selected must be the one that can maintain the high aspect ratio of the NC. Solvent casting, filtration methods maintain the aspect ratio of the NC but are not industrially viable method. On the contrary, extrusion and film making can be a commercial method where aspect ratio of NC reduces due to shearing forces offered by the rotating screws. New materials can always be explored by combining different forms of NC (type, chemical modification, changing the derivatives) with various elements as a better energy storage material.

Nanocellulose-Based Composites for CO_2 Capture

CO_2 is the biggest contributor of (around 75%) the greenhouse gas effect. Hence Carbon Capture and Storage (CCS) is highly essential to reduce CO_2 emission into the atmosphere. Recently, research is being more focused on production of biogas from organic materials, which mostly, is composed of 50–75% methane and 25–50% carbon dioxide.[108] Vehicle fuel should contain higher CH_4 content (above 95%) to reduce the CO_2 emissions. Various techniques like pressure swing adsorption, water scrubbing, and membrane technology are employed to upgrade the biogas quality. Membrane technology is found superior over others due to its high energy efficiency, easy processing, and potential for large-scale application.[109] However, a trade-off exists

between properties such as selectivity and permeability of the membranes as highly selective membranes have low permeability and *vice versa*.[110] Attention is paid more on facilitated transport membranes (FTM) for CO_2 separation as it has shown high selectivity as well as high permeance.[111] The nonreactive gas like CH_4 will permeate by solution diffusion mechanism whereas CO_2 can selectively be permeated through the membrane with the help of carriers present in the polymer membrane. Relative humidity has been found to be a critical factor, which must be taken into consideration during the development of membranes for CO_2/CH_4 mixtures as it enhances the CO_2 permeation as well as improves the CO_2/CH_4 selectivity (See Table III).[112]

CNC films possess superior barrier properties under dry conditions. CNC chain contains pendant hydroxyl group, the film of which gets swollen in humid atmosphere. This characteristic makes CNC more eligible as a filler material in polymeric membranes to expedite the transport of CO_2.[32] However as CNC acts as a reinforcing agent in CNC-based nanocomposites, at high concentration levels it restrains the swelling mechanism thus limiting the amount of moisture uptake.[113] Jahan *et al.* performed experiments by varying the concentration of CNC in PVA membranes at a constant pH and found it to positively affect the membranes performance. The optimal concentration of CNC in the PVA membrane was found to be 1 wt%. The improvements in the CO_2 permeation and CO_2/CH_4 selectivity of the membrane were observed at concentrations below 1 wt%. On the other-hand, a decrease in these properties were observed at concentrations above 1 wt%, which the authors attributed to the increase in crystallinity or decrease in moisture uptake. A significant increase in the thickness of the membrane was another drawback.[32] The separation performance of PVA/CNC are found comparable with PVA/CNT membranes.[114] This reveals the fact that NC has a commercial potential for producing advanced gas separation membranes. Feed pressure as well as pH levels of the suspension play key roles in the membranes performance (Figure 7) as the permeance is found to improve by a magnitude of four when the pH is 10 as compared to pure PVA membranes.[32]

It is experimentally shown that pure micro fibrillated cellulose films (MFCs) or MFC/Lupamin nanocomposite membranes display very high (above the 2008 Robeson's upper bound) separation performance for CO_2/CH_4 system.[110,115]

PROCESSING TECHNIQUES AND CHALLENGES

It is pertinent here to note that NCs are extremely difficult to disperse in polymers due to their intermolecular interactions. It is

Table III. Comparison of Separation Performance of Various Membranes

Membrane	Relative humidity	Feed pressure (bar)	Permeability/Permeance	Selectivity (CO_2/CH_4)	Reference
PVA membrane	-	5	12.9 Barrer	25	32
PVA/CNC membrane	100%	5	0.27 m^3 (STP)/ (m^2 bar h) or 70 Barrer	39	32,112
PVA/CNC membrane	-	15	0.11 m^3 (STP)/(m^2 bar h).	31	112
PVA/CNC membrane	30%	-	0.004 m^3 (STP)/ (m^2 bar h).	6	112

still remaining a challenge to optimize its dispersion. Many authors have focused their research in ensuring its effective dispersion in polymer matrices. *In situ* polymerization and post polymerization compounding are two commonly used methods used to incorporate NCs into polymer matrices.[116] During *in situ*

polymerization, a solvent is chosen in such a way that the monomers are soluble in it and the NCs disperse fairly easily leading to the formation of percolation networks. However, in certain cases crosslinking reaction occurs between the monomers and NC. On the other hand, for post polymerization compounding, water is
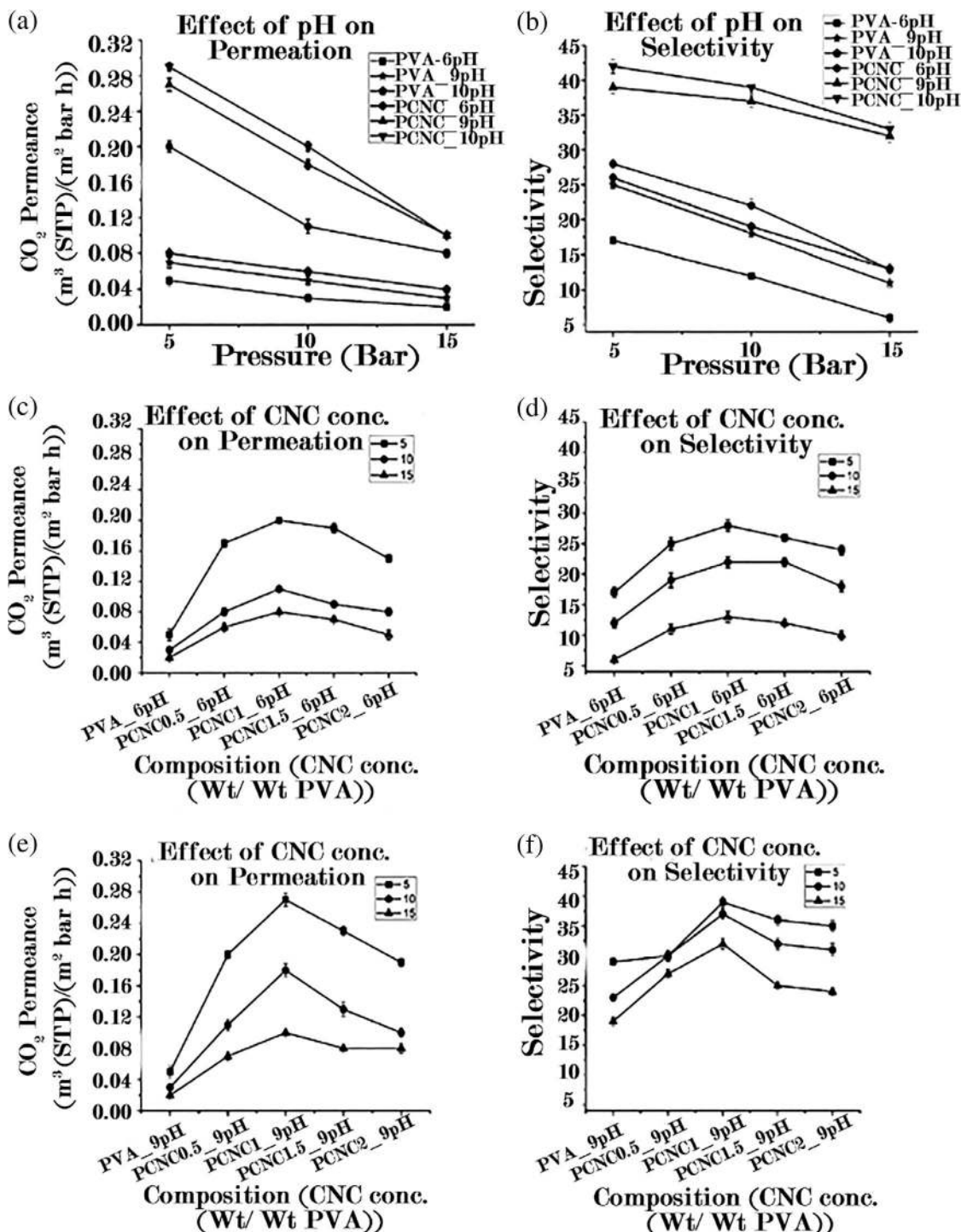

Figure 7. (a), (b) The effect of pH on the permeation and selectivity of the membrane (c), (d) show the effect on permeation and selectivity of CO_2 over CH_4 with changing concentrations of CNC at pH level 6 while figures, (e), (f) show the effect on permeation and selectivity of CO_2 over CH_4 with changing concentrations of CNC at pH level 9. Reproduced with permission.[32]

used as a processing medium to incorporate NCs into the polymer matrices.[117–119] A major limitation here is that only water-soluble polymer matrices can be used. The dispersion of NCs in organic solvents can be carried using strong sonification.[13,120,121] Manufacturing of such nanocomposites in liquid media is always preferred as the dispersion of the particles in the aqueous media is fairly good. However, film casting is not an industry-scale process. To produce cellulose nanocomposites for commercial purpose, a processing technique must allow manufacturing of these materials from laboratory to industrially viable method. To look at it with an industrial aspect, the melt processing techniques like extrusion and injection molding are very promising as they are very economical, simple, green, and does not require organic solvents. But there are two important issues that must be addressed before these processes are taken for mass production. First, as mentioned before, is the aspect ratio that reduces due to shear forces offered by the screws. The second issue is the agglomerate formation of nanofillers. Even upon drying, NC reagglomerates and makes it difficult to disperse homogeneously in the molten polymer during extrusion.[122] Apart from that, there is an inherent incompatibility of the hydrophilic nanocellulose with petro-based hydrophobic polymers.[123] The interparticle interaction causes aggregation of NC in nonpolar matrices due to the formation of additional hydrogen bonds between them. In the recent past, some attempts were made to work on these processing issues.[124–128] But it still needs a great attention to resolve these concerns.

CONCLUSIONS

We surveyed the recent developments in nanocellulose-based composites employed in energy conversion and conservation devices. The research in making nanocellulose reinforced composites as energy conversion devices has speeded up. The recent research reveals that nanocellulose is a promising piezoelectric material for sensors and actuators. The piezoelectric performance of nanocellulose/$BaTiO_3$ is found at par with PVDF-based composites. Research is progressing in the direction of orienting the CNC crystals in the film and understanding the effect of plasticisers on the piezoelectric performance of biobased nanocomposites. CNCs having high optical haze can be employed in enhancing power conversion efficiency of solar cells. Shelf-life and stability of nanocellulose-based solar cells in humid atmosphere should be enhanced.

Nanocellulose, being sustainable and biodegradable with remarkable and tailoring properties, ubiquitously proves to be a demanding substrate in making flexible electrodes and separators in LIBs and supercapacitors. To improve the capacity and stability of LIBs, research is more accelerated to enhance the porosity and homogeneous surface pore distribution. To enhance the energy density further, the design and manufacturing aspects of nanocellulose-based aerogels and 3D structures are also being explored recently. More efforts in the development of industrially viable processing technique that can manufacture big-sized electrodes are required. For CO_2 capture, facilitated transport membranes made of nanocellulose reinforced composites have displayed very high separation performance for CO_2/CH_4.

Hydrophilicity of nanocellulose is well exploited in such applications.

Definitely, challenges are there and more efforts are required to warrant such sustainable materials in energy applications keeping in mind the environmental protection. At a first place, high manufacturing cost and time are still the concerns with nanocellulose production. New ways to produce nanocellulose with large scalability and low cost should come up.

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