Isolation and characterization of cellulose and cellulose nanocrystals from sugar cane bagasse and development of dye-sensitized solar cell fabrication by using their sources

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***Abstract*—The deliberate study of biopolymer electrolytes for electro - chemical uses, such as dye-sensitive solar cells, batteries, super capacitors, etc., has begun recently. One of the biodegradable polymers, cellulose has a variety of applications in medicine and pharmaceutical administration. In medicine and medication delivery, cellulose is one of the biodegradable polymers with a variety of functions. These are the main factors driving the increase in interest in these subjects, for which synthetic polymers have historically been the material of choice. According to the literature surveys, solid polymer electrolytes are typically made using ammonium salts, inorganic acids, and alkali metal salts. The main reasons for the increase in interest in these subjects, for which synthetic polymers have historically been the favoured materials, are those mentioned above. Cellulose (CL) was extracted from sugar cane bagasse using sodium hydroxide as an alkaline agent, followed by sodium chlorite as bleach, and cellulose nanocrystals (CLN) were created using acid hydrolysis from the cellulose derived from sugar cane bagasse. Both CL and CLN were characterized using thermal, spectroscopy, and diffraction methods. Gel polymer electrolytes were created using CL and CLN. In order to make cellulose gel electrolytes (CGE) and cellulose nanocrystals gel electrolytes, dimethyl sulfoxide (DMSO), a cheap and environmentally acceptable solvent, is utilized (CNGE). CNGE has efficiency of 0.75, which is optimally greater than that of CGE of 0.43.**

***Keywords*—Cellulose nanocrystals; Cellulose; Gel Electrolyte cellulose nanocrystals; Gel Electrolytes**

I. INTRODUCTION

Depleting fossil resources and growing energy demands are major causes to research alternative energy sources in the modern period. The increasing popularity of electronic devices and electric vehicles has increased the demand for cost-effective, efficient, and safer electrochemical technologies. Liquid electrolytes are increasingly being used in commercial products. Liquid electrolytes increase the size and weight of certain devices, lowering their specific power densities and specific energy. Liquid electrolytes, regardless of solvent type, have a fundamental barrier for long-term operation in device applications due to evaporation and leakage. Gel electrolytes, also known as quasi solid state electrolytes, have lately acquired popularity due to their long-term stability and improved mechanical properties. The use of biopolymers in electrolytes and electronics can be a superior alternative for some toxic substances, notably in lithium ion batteries, super capacitors, solar cells, and other applications. Biopolymers have sparked a lot of attention as a result of the detrimental effects of many conventional polymers.

Biopolymers are comparatively great and beneficial since they are affordable, abundant, non-toxic, ecologically friendly, soluble in water, renewable, and the most practicable solution for lowering dangerous commercial polymers. Biopolymers have been widely employed in a number of applications without negatively impacting the environment. Biopolymer-based electrolytes are now widely used in electrochemical device applications [1,2,3].

Dye sensitized solar cells (DSSCs) are a hybrid photovoltaic (PV) technology of the third generation. The first two generations of PV technologies dominated the PV industry since their inception, however they are not widely used because to high production costs and environmental concerns[4]. Because of its cheap production cost and minimal environmental effect, DSSC has been the most investigated PV technology during the last two decades. Since their creation, electrolyte formulations have been a key barrier to their commercialization, affecting the long-term stability of these devices. To address stability issues, several electrolyte compositions are studied and utilized in DSSC devices[5].

The electrolyte is a critical component in dye sensitive solar cells. It influences cell stability and performance because it regulates charge transfer kinetics. Electrolytes are classified into three types: liquids, quasi-solid or gel state, and solid state. Traditional electrolytes are made comprised of a redox pair, a few additions, and an organic solvent. The I- /I_3^- pair is the most common redox mediator. Br-/ Br_2[31], SCN-/$(SCN)_2$[32], SeCN-/$(SeCN)_2$[33], or modified bipyridyl cobalt(III/II)[34] redox couples were also tested in DSSC. Cobalt complexes get a reported efficiency of 13%, making them a viable alternative to traditional redox couples[6].

The very first DSSC reported an efficiency of 7 - 8% to use a liquid electrolyte composed of the organic solvent an iodide / triiodide redox combination. Because of its properties such as high carrier collection, great immersion, relative high stability, cheap cost, and simple preparation, the iodide - triiodide (I_3^- / I^-) electrolyte system has shown to be the best redox couple[7].

DSSCs with liquid electrolytes have the highest solar-to-electrical conversion efficiency, but the fundamental obstacle to their successful commercialization is leakage and sealing problems that affect long-term device stability. Gel electrolytes, also known as quasi-solid electrolytes, have a composite membrane that serves as a support structure for the additional inorganic salts and solvent. The polymer matrix used to generate a three - dimensional network can either be inert or integrating. The cations and anions in inert gel electrolytes, such as poly(vinylidene fluoride) (PVDF) and poly(acrylonitrile) (PAN), can freely flow in the solvent (liquid phase). The binary phase (liquid and solid) in gel electrolytes containing coordinating polymers, such poly (ethylene oxide) (PEO), is where the ionic transport takes place[8].

Solid state electrolytes provide a few benefits, but they also have low conversion efficiency because the photo-anode and the electrolyte have poor interfacial contact. So, due to greater sealing ability and superior stability, quasi solid state or gel state electrolyte may become a workable substitute for liquid and solid state electrolytes.

Gel state electrolytes have both the cohesiveness of a solid and the dispersive characteristic of a liquid. Due to its particular quality, the gel can be used in polymer electrolytes, among other things. Three main techniques are frequently utilised to create gel state or quasi state electrolytes.
There is a Liquid electrolyte are gelatinized employing inorganic materials and Liquid electrolytes are gelatinized using organic gelators[9].

Many synthetic polymeric hosts, including as poly vinyl alcohol (PVA), polyethylene oxide (PEO), poly - styrene, poly methyl meta acrylate (PMMA), and poly vinyl chloride (PVC), have been utilized as gelators to date. Gel electrolytes made from synthetic polymers have several benefits over liquid electrolytes. However, due to environmental concerns and the need to lower production costs, biodegradable polymers are the best solution for the current environmental situation.

The current trend and benefit over synthetic polymers is the use of biopolymers in the manufacture of electrolytes. Biopolymer-based gel electrolytes have a very high conductivity and offer improved connection between the electrode and the electrolyte. Recently, biopolymers were employed for electrochemical applications, particularly dye-sensitive solar cells, including cellulose[35], pectin[36], carrageenan[37], cereal starches[38], chitosan[39], xantham gum[40], and gellan gum (DSSCs) [10].

Cellulose is the most commonly occurring biomass substance encountered in nature. It is found in a wide range of living species including plants, animals, and bacteria[11]. The construction of plant cell walls depends on cellulose, a fibrous, stiff, water-insoluble polymer. It is a high molecular weight linear homopolymer made up of 1, 4-anhydro-D-glucose units that are corkscrewed 180 degrees in relation to one another. The biomass substance that occurs most frequently in nature is cellulose. Numerous living species, including microbes, plants, and mammals, contain it. The fibrous, stiff, water-insoluble polymer known as cellulose is crucial for the development of plant cell walls[12]. It consists of 1, 4 - anhydro - D-glucose unit that are corkscrewed 180 ° in respect to one another to form a linear homopolymer with a high molecular weight. The sugar rings are linked by glycosidic oxygen bridges as a result of the condensation reaction that connects the monomers[13]. Cellulose is created at the site of biosynthesis as individual molecules that spin in a hierarchical order, and it also occurs in nature as individual molecules that spin in a hierarchical order. These are the primary factors driving the rise in interest in cellulose-based products besides food[14]. For electrochemical uses including dye - sensitized solar cells, batteries, and super capacitors, polymer electrolytes have received a lot of attention[15].

Traditional liquid electrolytes based on organic solvents (such acetonitrile or 3-methoxypropionitrile) have been used in DSSC, but some organic solvents are dangerous and/or explosive. Due to environmental and safety problems, these are the drawbacks of these solvents in terms of practical application. Water-based solvents have therefore been investigated as an alternative to organic-based solvents[16,17]. The use of water-based electrolytes by DSSC protects them against performance degradation brought on by water intrusion as a result of inadequate sealing and is environmentally friendly. However, regardless of the kind of solvent, liquid electrolytes have a fundamental limitation for long-term operation due to their evaporation and leakage[18]. Polymer gel electrolytes have recently garnered a lot of attention due to their remarkable mechanical properties and long-term durability. If the advantages of polymer gel electrolytes and water-based electrolytes could be combined, an eco-friendly, incredibly dependable electrolyte that resists both solvent and water leaks would be possible[19].

Making nanocomposites polymer gel electrolytes out of cellulose has garnered a lot of attention lately. Sugar cane bagasse is a possible alternative to other cellulose.

The objective of this study is to separate cellulose and cellulose nanocrystals from sugarcane. Lithium iodide was used to create gel electrolyte for DSSC application. The purpose of this study is to separate cellulose and cellulose nanocrystals from sugarcane. Cellulose and cellulose nanocrystals were developed with lithium iodide to create gel electrolyte for DSSC application.

II. MATERIALS AND METHODS

Bagasse was obtained from a sugarcane factory in Mysore, India. Sdfine Chemicals (India) supplied the sodium sulphite and sodium hydroxide. Sigma Aldrich provided the sodium chlorite, while Fisher Scientific (India) provided the sodium hypochlorite. All compounds were utilized without additional purification, but at the necessary concentrations.

2.1 Isolation of cellulose from sugar cane bagasse (SCB)

Cellulose is extracted from sugar cane bagasse using an alkali technique[20]. SCB were pulverized and boiled for 4 hours before being steeped in 4% sodium hydroxide for 4 hours before being washed with distilled water to pH neutral. The final product was dried at room temperature for two days. The overall yield of cellulose achieved was 70-75%.

2.2 Extraction of cellulose nanocrystals from cellulose (CLN)

Following the method recommended by Ghazuet al[21], cellulose nanocrystals (CNC) were manufactured. Using an orbital shaker, 10g of cellulose was suspended in 100 ml of 36% H_2SO_4 and incubated for two days at 40°C with continual stirring at a speed of 500 rpm (Scigenics Biotech Pvt, India). After the suspension had been acid hydrolyzed, it was centrifuged after being cleaned with distilled water. Washing and centrifugation were carried out one after the other until the pH of the washing was neutral. The final residue was freeze-dried and kept in a desiccator after drying. The overall CNC yield was between 65-70%.

2.3 Preparation of electrolytes

The liquid electrolyte (E_L), which was made by combining 1M of lithium iodide (LiI) and 20mM of iodine (I_2) in distilled water. A appropriate amount of cellulose was added to the distilled water for the gel polymer electrolyte (Eg), which was then heated to 60˚C for about 20 minutes to dissolve and gelatinize the cellulose. After cooling, 1M of LiI and 20mM of I_2 were added to the abovementioned solution.

2.4 Characterizations

Using a Thermo Nicolet FTIR spectrometer, the FT-IR spectra of cellulose and cellulose nanocrystals were measured (Model 5700, Madison, USA). Every spectrum was précised between 4000 and 650 cm^{-1}. Spectra were recorded with a resolution of 4 cm^{-1} and 64 spectra were averaged. The X-ray diffractograms of the cellulose and cellulose nanocrystals were measured using Rigaku Miniflex – II X-ray diffractometer with Ni filtered, CuKα radiation of wavelength λ=1.5406 ˚A with a graphite manochromator. The parameters used for the recordings were 30 kVand 15 mA. The samples were scanned in the 2θ range 4-40° with a scanning speed of 5 ° / min and step size of 0.02.Differential scanning calorimetric measurements were carried out using a thermal analyst 2100 system (Model DSC 2910, TA Instruments, USA). Less than 10 mg of freeze dried samples were weighted and hermetically packed inside aluminium DSC sample pans. Each pan was heated from -20 ° C to 220 ° C at a heating rate of 10 ° C/min. A pure Indium sample was used for calibration. The TA Instruments software was used to determine the enthalpy change (ΔH) during the process. The thermal stability of cellulose and cellulose nanocrystals was determined by thermo gravimetric analysis (Model, TGA 2910, TA instrument USA). During the measurements, a nitrogen gas flow rate of 10 ml/min was maintained. Approximately 10 mg of the samples were analysed at temperatures ranging from 30° C to 600° C at a heating rate of 10° C/min.

III. RESULTS AND DISCUSSION

3.1 FT-IR analysis

FTIR spectra of sugarcane bagasse, cellulose, and cellulose nanocrystals are given in Figure 1. The infrared absorption bands of cellulose and cellulose nanocrystals along with its band assignments are given in Table 1. According to the FTIR spectrum, sugarcane bagasse has a number of peaks that are not present in the cellulose and cellulose nanocrystals spectra. At a wavelength of 1252 cm^{-1}, the aryl group in lignin began to display a C-O stretching vibration. The aromatic ring's C=C stretching vibration is seen at 1511 cm^{-1} in lignin. After acid hydrolysis, the O-H and C-H stretching vibrations were assigned peaks at 3451 cm^{-1} and 2899 cm^{-1}, respectively. The O-H vibration of absorbed water was found to have the highest absorption at 1644 cm^{-1}. The peak for C-H and C-O vibrations limited in cellulose polysaccharide rings is at 1382 cm^{-1}. The absorption peak at 1060cm^{-1} represents the vibration of the C-O-C pyranose ring.[22, 23, 28].

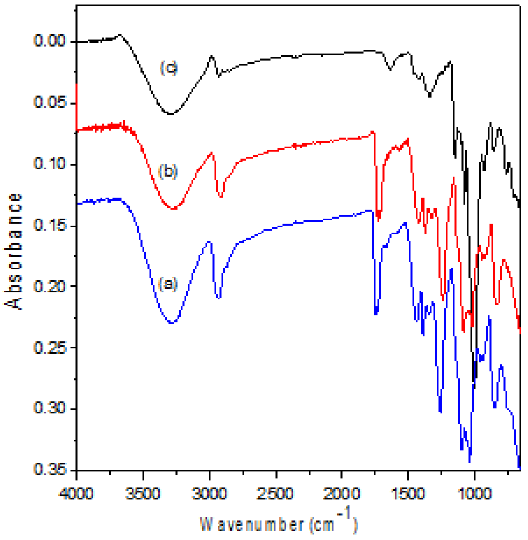

Fig. 1- FTIR analysis of (a) sugar cane bagasse (b) cellulose (c) cellulose nanocrystals.

Table 1: Characteristic IR absorption peaks of SCB, CL & CLN are given in Table 1.

Peak assignment	SCB	CL	CLN
-OH (stretching)	3450	3452	3458
C=O (stretching)	1252	1254	1260
-OH (bending)	1630	1650	1690
C - O (st) in C - O - H	1145	1149	1158
C - O (st) in C – O - C	1003	1012	1094
C - O (bend) (c–o-c ring vibration in cellulose)	1060	1065	1075

3.2 XRD analysis

X-ray diffraction analysis was used to examine the crystallinity of cellulose and cellulose nanocrystals. Figure 2 depicts an XRD peak of cellulose and cellulose nanocrystals and XRD parameter are mentioned in table 2. Changes in the diffraction pattern of CLN produced following acid hydrolysis of CL were investigated. The XRD pattern of CL did not differ significantly from that of their respective CLN. Moving from CL to CLN, however, resulted in a modest rise in relative intensity and a minor expansion of the band. Cellulose had three diffraction peaks at 2θ = 14.6°, 21.2°, and 23.8°. The strength of the peaks increases dramatically after acid hydrolysis of cellulose, as does the crystallinity of the cellulose [24,29].

Table 2: XRD parameter of CL and CLN

Compounds	Intensity	% Crystallinity	% Crystallinity Index
CL	1600	51.6	0.45
CLC	2600	58.8	0.75

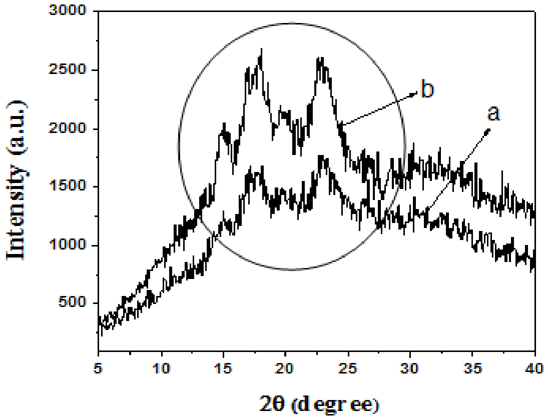

Fig. 2- XRD analysis of (a) cellulose (b) cellulose nanocrystals.

3.3. Differential scanning calorimetric analysis (DSC)

DSC thermograms of CL and CLN are shown in Figure 3. DSC analysis allows for the detection of numerous thermal transitions that occur in CL & CLN as the temperature rises. Figure 3 depicts DSC thermograms of CLN synthesized using H_2SO_4. For nanocrystals samples, large endothermic peaks were found in the temperature ranges 100-160˚C. The evaporation of free and bound water in CL & CLN causes these endotherms. Because of its hydrophilic nature, cellulose usually includes some moisture. The majority of this water will evaporate when heated. Physical desorption of water occurs at temperatures less than 150˚C, and thermal dehydration also occurs at temperatures between 100 and 160˚C. The glass transition temperatures for cellulose and cellulose nanocrystals were discovered to be 100°C and 110°C, respectively. On CLN, the glass transition temperature seemed to have increased considerably. The melting points of cellulose and cellulose nanocrystals were determined to be 189°C and 210°C, respectively. The comparable melting enthalpy (ΔHm) determined was 56.2 J/g to 58.6 J/g. The increase in melting enthalpy also indicates improved molecular interactions, resulting in better cellulose nanocrystals binding[25,30].

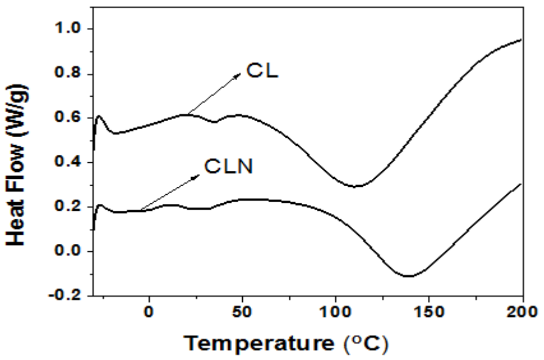

Fig. 3 - DSC analysis of (a) cellulose (b) cellulose nanocrystals

3.4. Thermogravimetric analysis (TGA)

TGA was used to investigate the thermal properties of cellulose and cellulose nanocrystals, and the DTGA curves are presented in Figure 4. Thermal degradation of cellulose and cellulose nanocrystals was studied at temperatures ranging from 30° to 600° C. There are three stages to the breakdown of cellulose and cellulose nanocrystals. The hydroxyl groups are first dehydrated during the breakdown process. The synthesis of volatile organic chemicals is then followed by the creation of conjugated unsaturated polyene structures (Tubbs & Ting, 1973). When the temperature rises over 450°C, the second stage of degradation begins, producing low molecular weight molecules such as alkenes, alkanes, and aromatics. Carbonaceous residues will develop over 500°C.In the present case it can be observed that thermal decomposition temperature of cellulose nanocrystals (243˚C) has shifted slightly toward lower temperature compared to cellulose (287˚C) [26].

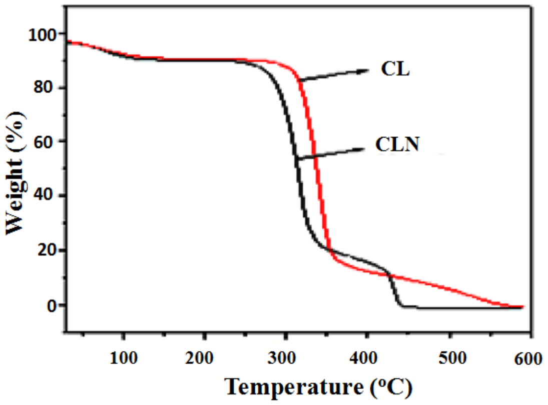

Fig. 4 - TGA analysis of (a) cellulose (b) cellulose nanocrystals

3.5. DSSC Fabrication and Characterization

DSSC parameter of CGE and CNGE electrolyte results are given in table 3. DSSC was performed on the two aqueous systems, Gel and Liquid electrolytes. Gel electrolyte has slightly greater conversion efficiency than liquid electrolyte. However, the water in these systems causes limited ionic conductivity, which leads to low conversion energy and insignificant DSSC performance. Figures 5 and 6 clearly show the improvement in efficiency and current density for the gel electrolyte system. This might be because cellulose nanocrystals - based gel electrolyte has a better conductivity than liquid electrolyte. CNGE has a greater conductivity of 8.92 S/Cm than CGE electrolyte (8.52 S/Cm). When compared to CGE - based DSSCs (1.63%), CNGE - based DSSCs have the greatest conversion efficiency of 1.98%. However this is the attempt to use the prepared cellulose nanocrystals in DSSC application [27].

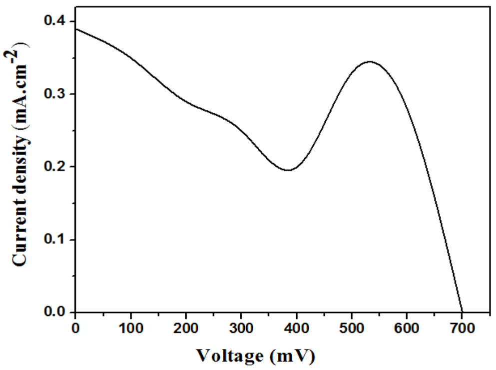

Fig. 5 – Photo current Density V/S cell potential for DSSC fabricated with liquid electrolyte.

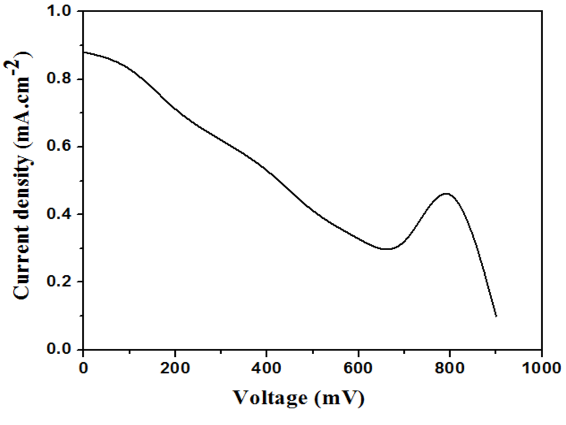

Fig. 6 - Photocurrent Density V/S cell potential for DSSC fabricated with Gel electrolyte.

Table 3. DSSC parameter of CGE and CNGE electrolyte

Electrolyte type	Voc (mV)	Jsc (mA*cm^{-2})	FF	η
CGE	690	0.38	0.32	0.083
CNGE	900	0.88	0.6	0.4752

IV. CONCLUSIONS

Cellulose was isolated using an alkali technique from sugar cane bagasse, and cellulose nanocrystals were separated using an acid hydrolysis approach. Spectral, diffraction, and thermal methods were used to describe cellulose and cellulose nanocrystals. Later, a water-based gel polymer electrolyte encapsulating cellulose and cellulose nanocrystals was produced. A dye-sensitized solar cell was built with a water-based liquid electrolyte, cellulose and cellulose nanocrystals, and a water-based gel electrolyte, and it was analyzed with a sun simulator at 100 mW/cm^2. The J - V graph clearly shows that the gel electrolyte system's efficiency and current density have increased. This might be because cellulose nanocrystals-based gel electrolyte has a better conductivity than liquid electrolyte.

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