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# Carboxymethyl cellulose-based materials as an alternative source for sustainable electrochemical devices: a review

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In electrochemistry, bio-based materials are preferred over the traditional costly and synthetic polymers due to their abundance, versatility, sustainability and low cost. One of the bio-based polymers is carboxymethyl cellulose (CMC) which has become an overarching material in electrochemical devices pertaining to its amphiphilic nature with multi-carbon functional groups. Owing to its flexible framework with fascinating groups on its surface like hydroxide ( $-\text{OH}$ ) and carboxylate ( $-\text{COO}^-$ ), CMC is able to be modified into conducting materials by blending it with other biopolymers, synthetic polymers, salts, acids and others. This blending has improved the profile of CMC by exploiting the ability of hydrogen bonding, swelling, adhesiveness and dispersion of charges and ions. These properties of CMC have made it possible to utilize this bio-sourced polymer in several applications as a conducting electrolyte, binder in electrodes, detector, sensor and active material in fuel cells, actuators and triboelectric nanogenerators (TENG). Thus, CMC based materials are cheap, environment friendly, hydrophilic, biodegradable, non-toxic and biocompatible which render it a desirable material in energy storage devices.

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## 1. Introduction

Polymers, giant molecules containing multiple repeating units, are equally important for their technological applications as well as from a fundamental scientific point of view. Usually, polymer materials are considered as insulators, however, they could be upgraded into conducting materials.<sup>1,2</sup> Modified

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chemical properties of ionic liquid functionalized biopolymers.



polymer conducting materials are envisioned as host materials in energy storage media in the near future. These have been widely used in sensors, batteries, fuel cells, capacitors, photo-electrochemical solar cells and electrochromic displays.<sup>3</sup> They have stable structure and low volatility, therefore, can be used in modern technology devices.<sup>4,5</sup>

Ion conductivity behavior of polymers was first uncovered by Wright in 1975 (ref. 6) who discovered the ionic conductive behavior of polyethylene oxide-alkaline metal ion complex. There were a lot of struggles at that time to improve the ionic conductivity of polymer electrolytes and making facile the applications of polymers in power applications. Much attention was paid on synthetic polymer such as polyethylene oxide (PEO) and polyvinyl alcohol (PVA).<sup>7,8</sup> But these synthetic polymers are costly and depleting petroleum resources. Comparatively, natural polymers like cellulose and cellulose derivatives are ecofriendly, abundantly available and low-priced.<sup>9,10</sup> One of such exciting polymers is carboxymethyl cellulose (CMC).<sup>11</sup>

CMC is a polysaccharide comprising of fibrous tissues of plants. It is water soluble, low-cost polymer containing hydroxyl and sodium carboxymethyl groups ( $-\text{CH}_2\text{COONa}$ ).<sup>12,13</sup> It has emerged as a valuable chemical due to its anticipated properties such as biodegradability, nontoxicity, high hydrophilicity, biocompatibility and excellent film forming ability.<sup>14</sup> It exhibits variety of applications in textile, drugs, flocculation, food processing, detergents and many more.<sup>15,16</sup>

Role of CMC in electrochemistry is based on its parent molecule "cellulose" which is a biodegradable natural biopolymer with linear polysaccharide chain. The acidification of cellulose yields its linear bulky derivative 'CMC'.<sup>17,18</sup> It is an

abundant carbon resource due to its multi-carbon functional groups which could be modified to obtain dense carbon conducting framework.<sup>19,20</sup> However, as a single polymer, CMC has the limited stability and miscibility in electrochemical devices.<sup>21</sup> To enhance the efficiency, CMC has been mixed with other biodegradable polymers like PVA, PEO, cellulose, hemi-cellulose, chitosan, kappa carrageenan (KC) and so on. The mixing of these polymers with CMC tend to increase its physicochemical properties such as miscibility, tensile strength, ionic conductivity and reduce the crystallinity.<sup>22</sup>

Herein, we will initially present CMC applications in energy storage devices as an electrolyte or binder in detail. After that, applications of CMC in energy conversion and generation devices such as fuel cells and TENG will be discussed. Lastly, we will discuss its applications in electrical devices like biosensors and actuators. Moreover, we are well aware of recent reviews on role of biopolymers in electrochemistry.<sup>23,24</sup> But to the best of our knowledge, there is no published review on applications of CMC based materials in electrochemistry, specifically.

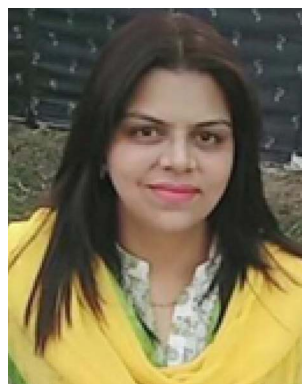
## 2. CMC based materials in energy storage devices as electrolyte/binder

In energy storage devices, energy is stored in different forms such as electromagnetic, electrochemical, chemical, potential, kinetic and thermal.<sup>25</sup> In view of, power density, energy density, technical maturity and cyclability rechargeable batteries have been popularized.<sup>26</sup> Among them, CMC has found wide range of applications as an electrolyte, binder for electrode in batteries and cells that have been discussed here in detail.



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## 2.1. General advantages of solid polymer electrolytes (SPEs) over liquid electrolytes

Traditionally, liquid electrolytes have been used in electrochemical applications because they are conductive even at low temperature. But they have certain drawbacks which make them unsuitable for electrochemical devices such as leakage, deterioration, instability and so on.<sup>27</sup> Moreover, they could react with electrode, lead to corrosion and decrease the life span of the device.<sup>28</sup> Additionally, boiling point of solvent restricts the temperature of the device, showing lower electrochemical firmness.<sup>29</sup> With the discovery of solid polymer electrolytes (SPEs) in 1975,<sup>11</sup> these were predicted as suitable substitute for liquid electrolytes due to their better conductivity as well as improved mechanical and thermal stability (Fig. 1).<sup>29,30</sup> From there on, SPEs are preferred due to their high elasticity, low self-discharge, no leakage, easy processibility and good compatibility with electrodes.<sup>31</sup> The only serious disadvantage of solid electrolyte is their crystallinity but it can be solved by using organic or inorganic acids/salts.<sup>32</sup> Nowadays, SPEs have gained considerable attention due to their potent applications in energy density batteries, electrochemical cells, electrochromic devices and fuel cells.<sup>33</sup> But natural polymer electrolytes are preferred over earlier synthetic polymers due to low cost, biocompatibility and availability.<sup>28,34</sup>

## 2.2. CMC based blends as solid-state electrolyte

The use of cellulose and its derivatives as solid polymer electrolyte (SPE) is noteworthy because these are predicting green future unlike toxic and harmful materials. One of the derivatives of cellulose is CMC which has been extensively used as solid electrolyte in batteries and cells. CMC, when combined with other biopolymers or salts, has been showing excellent conductivity with cost-effectiveness which makes it desirable as electrolyte in energy storage devices. CMC based blends reported as solid-state electrolytes are briefly summarized in next sections.

**2.2.1. CMC and synthetic polymers blends.** In order to use the synthetic polymers with poor processibility and low mechanical properties in electrochemistry, they are hybridized with other materials such as CMC.<sup>35</sup> This could cause the collapse of polymer backbone during charge–discharge cycles resulting in their enhanced electrochemical power.<sup>36,37</sup> For example, blend of polyethylene oxide (PEO) with CMC (30/70 wt%) was observed to exhibit reduced crystallinity as obvious by XRD. The blend was reported to exhibit  $5.19 \times 10^{-5} \text{ S cm}^{-1}$  maximum electrical conductivity, minimum relaxation time and activation energy which make it a potent host matrix blend for SPE in energy storage devices.<sup>38</sup> Research group of Karaca used CMC as coating material with two intercalated vanadium surfaces of polypyrrole oxide and pencil graphite. The capacitance properties like galvanostatic charge discharge, potential recycling and electrochemical impedance spectroscopy (EIS) methods of composites were compared with coating prepared without additives. The addition of vanadium had significantly enhanced the specific capacitance and CMC was an enhancer of cyclic properties of composite. The improved specific capacitance was the result of homogenous distribution and synergetic effect of two vanadium mixed surfaces. The capacitance value was studied in different solutions such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ), lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) and  $\text{HBF}_4/\text{TBABF}_4$ . Results of both symmetric and asymmetric capacitors result were compared; the charge–discharge of asymmetric capacitor with composite coating was leading. The capacitor showed high energy density  $18 \text{ W h kg}^{-1}$ , high power density of  $0.43 \text{ kW kg}^{-1}$  at  $0.5 \text{ A g}^{-1}$  with potential range of 1.2 V of stable cycle life.<sup>39</sup>

**2.2.2. CMC and natural polymer synergistic blends.** The composites of CMC with other natural polymers are considered as state-of-the-art materials because of their low cost, high efficiency, environment friendliness and biodegradability. One of the polymers is kappa carrageenan (KC); an extractive mixture of sulfated polysaccharide from red algae. CMC and KC are hydrophilic polymers with anionic polysaccharide groups, have excellent water swelling ability due to their dissolution in

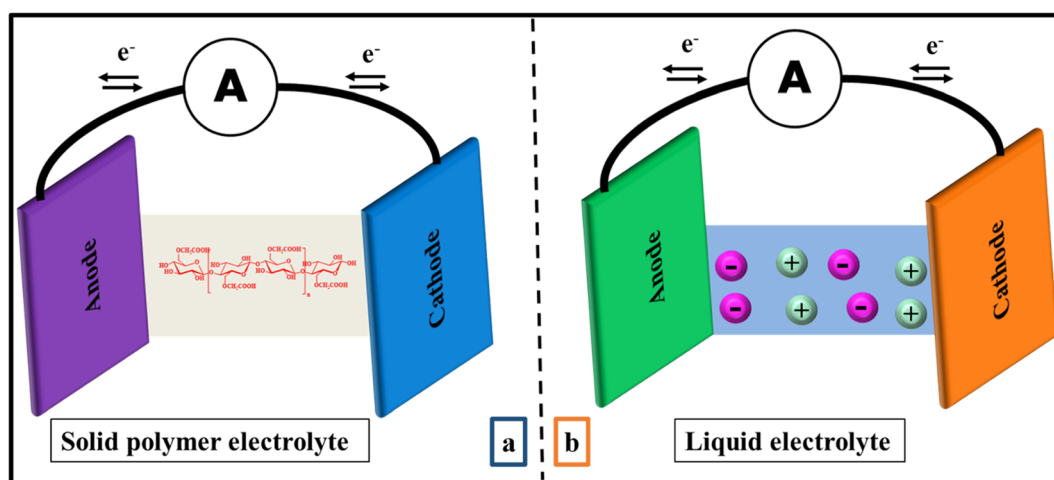


Fig. 1 Schematic illustration of electrolytes based on (a) solid polymer electrolyte (SPE) (b) conventional liquid polymer electrolyte in electrochemical storage devices.

water. Both are non-toxic, biocompatible, cost-effective, renewable and biodegradable polymers that have proved to be excellent materials for electrolyte system. CMC and KC blends with different molar ratios are reported as promising candidates for polymer applications in semiconductors as electrolyte systems. Further addition of ionic dopant and plasticizer can make these blends more worthwhile. Actually, the blending has caused an increase in the available space for chain mobility. Increase in ionic conductivity as a result of decrease in crystallinity has increased the potential of these blends in electrolytic system.<sup>40</sup> Moreover, the primary host for the development of novel bio-based electrolytes based on the combination of carboxymethyl kappa-carrageenan and CMC was carboxymethyl kappa-carrageenan.<sup>41</sup> The incorporation of CMC into carboxymethyl kappa-carrageenan was shown to be an effective method for enhancing material qualities such as conductivity. The highest ionic conductivity at room temperature was  $2.41 \pm 10^{-3} \text{ S cm}^{-1}$  with 30 wt% of the salt. The increase in cross-linking between polymers chains and the doping salt resulted in enhanced conductivity.<sup>42</sup> The excessiveness of charge carriers in the system of bio-based electrolytes also contributed to the conductivity. Using this electrolyte for the manufacturing of dye sensitized solar cells (DSSC) resulted in an efficiency of 0.13% under  $100 \text{ mW cm}^{-2}$  of light intensity.<sup>43</sup> Weerasooriya *et al.*, used CMC blend with hemicellulose, prepared with weight ratio of 2 : 3. The ionic conductivity and physiochemical properties were developed by using 1–5 wt% of lithium perchlorate ( $\text{LiClO}_4$ ) as doped salt. The highest tensile strength was obtained with 3 wt%, and ionic conductivity with 5 wt% of  $\text{LiClO}_4$ . The 5 wt% loading of  $\text{LiClO}_4$  in films was considered outstanding for ionic conductance.<sup>44</sup>

### 2.2.3. CMC blends with carboxylic acids as cross linkers.

The crosslinking of CMC with other carboxylic acids was investigated by different researchers. Pérez-Madrigal *et al.*, have used CMC based pastes and hydrogels with supporting salts and citric acid as cross-linker in solid state electrolysis. The characteristics of these electrolytes were optimized with the capacitive response of poly(3,4-ethylenedioxythiophene) electrodes. The specific capacitance of optimized hydrogels was increased by 81.5 and  $76.8 \text{ F g}^{-1}$  by cyclic voltammetry (CV) and galvanostatic charge and discharge as compared to paste. These electrolytes have potential to be used in solid electrochemical supercapacitors.<sup>45</sup> Badry *et al.*, stated that CMC with different concentrations of acetic acid and constant concentration of glycerol as plasticizer is a perfect choice for solid state electrolyte. The prepared composite films were characterized; UV-vis showed that prepared material three optical band gaps have reduced due to increase in acetic acid amount up to 5 wt%, new absorption band around  $1693 \text{ cm}^{-1}$  due to CMC/acetic acid interactions were indicated by FTIR. In  $^1\text{H}$  NMR, the disappearance of carbonyl group in some samples, EIS showed highest ionic conductivity of  $7.64 \times 10^{-6} \text{ S cm}^{-1}$  and thermal stability had been changed with varying acid concentrations and weight loss was observed in three stages of TGA curves.<sup>46</sup>

**2.2.4. Putative coordination of CMC and ammonium halides in proton conducting biopolymer electrolyte (BE) system.** In an electrolyte system, ions for conduction can be

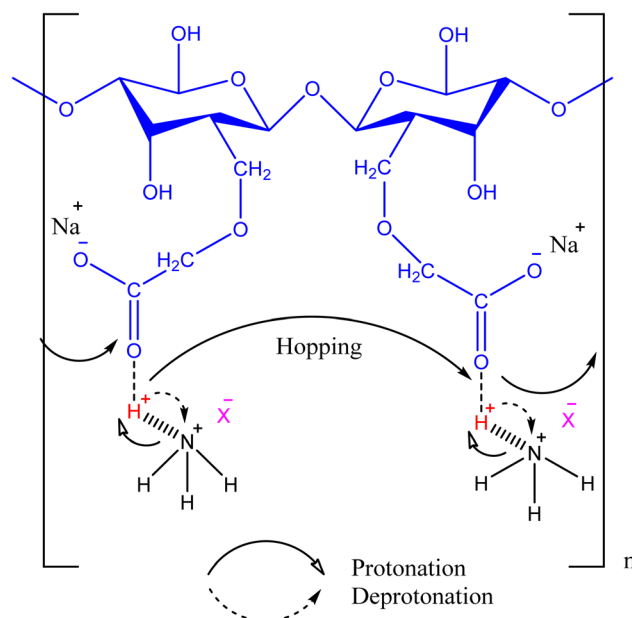


Fig. 2 A schematic representation of hopping mechanism involving protonation and deprotonation by the coordination of CMC with ammonium salts.

provided by polymer-salt complex. Bio-based polymers with ammonium salts provide good number of ions because the later have been reported as good proton donor in polymer matrix. A group of Isa *et al.*, has performed excellent work on the hydrogen ion conducting solid biopolymer electrolyte comprising CMC. When CMC was combined with propylene carbonate (PC) and ammonium chloride, prepared by solution casting method, the best conductance of  $(1.01 \pm 0.03) \times 10^{-2} \text{ S cm}^{-1}$  was achieved by composite containing 8 wt% of PC whose addition make the inverse relation of free ions due to weaker protonation with ionic conductivity. The surge in density number of ions until addition of 12 wt% of PC was confirmed by ionic conductivity, hopping method of mobility and diffusion (Fig. 2). PC facilitated the dissociation of  $\text{H}^+$  from ammonium chloride which had improved the electrolyte performance. The optimized composite when utilized in solid-state ionic cell of hydrogen, the performance of cell was quite good with discharge of 9 mA and recharge capacity was up to 9 cycles. The maximum discharge capacity was 2.7 mA h for 20 minutes which indicated the stability of composite in electrochemical devices.<sup>40</sup>

In another study by the same research group,  $\text{NH}_4\text{Br}$ -doped CMC served as the polymer host in the biopolymer electrolyte (BE) system. Analysis of the BE system's ionic conduction has been carried out using EIS and the most conducting sample was found to contain 25%  $\text{NH}_4\text{Br}$ . When different concentrations of plasticizer were introduced to the BE system, the ionic conductivity increased to  $3.31 \times 10^{-3} \text{ S cm}^{-1}$ . Proton batteries may be made using CMC based BE systems with high conductivities, according to linear sweep voltammetry (LSV) measurements. In comparison to previous studies that used polymer electrolytes in their solid-state batteries, these solid-state proton





batteries produced higher open-circuit voltages (OCVs) of 1.36 and 1.48 V at room temperature and outperformed previous studies that used polymer electrolytes in their solid-state batteries.<sup>41</sup> On the same ground, Yang *et al.*, developed proton conducting BE by combining different  $\text{NH}_4\text{Br}$  compositions (wt%) with biopolymer materials CMC. It has been revealed that the conducting material is mostly available proton ( $\text{H}^+$ ) in this study, as verified by FTIR and transference number measurement (TNM) analyses. The  $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}/\text{BE}/\text{MnO}_2$  design of a rechargeable proton conducting BE battery generated an all-out open circuit potential (OCP) of 1.36 V at room temperature and demonstrated excellent rechargeability.<sup>42</sup>

Samsudin *et al.*, also investigated CMC based BE systems containing  $\text{NH}_4\text{Br}$ . FTIR spectroscopy revealed a putative coordination relationship between CMC and  $\text{NH}_4\text{Br}$ , which was validated by the Grotthuss mechanism. The BE sample containing 25%  $\text{NH}_4\text{Br}$  had the maximum ionic conductivity at room temperature ( $1.12 \times 10^{-4} \text{ S cm}^{-1}$ ) and the least weight loss as evidenced by TGA. Ionic transference number of mobile ions determined by direct current polarization technique was 0.98, indicating that conducting species are ions ( $\text{H}^+$ ). The BE was electrochemically stable up to  $1.42 \pm 0.01 \text{ V}$ , making it appropriate for proton batteries.  $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}/\text{BE sample}/\text{MnO}_2$  rechargeable proton-conducting BE batteries were made. The proton battery had a starting cell potential of 1.52 V and a constant OCP of 1.36 V. It was recharged 10 times without losing cell potential.<sup>43</sup>

**2.2.5. CMC based polymer nanocomposites.** CMC based polymer nanocomposites serve as efficient electrolytes due to their monodispersity and reduced crystallinity. CMC extracted from kenaf bast fiber was reported to prepare BE system by mixing with an ionic liquid (1-butyl)trimethylammonium

bis(trifluoromethylsulfonyl)imide, ammonium acetate and silica nanofiller. The amount of silica nanofiller influences the conductivity of films. The highest conductivity ( $8.63 \times 10^{-3} \text{ S cm}^{-1}$ ) and electrochemical stability (3.4 V) were observed with 1 wt% of silica.<sup>47</sup> Gold nanoparticles produced from natural leaves extracts of *Ricinus communis*, *Solanum nigrum* and *Morus nigra* have also been reported for BE systems. Results showed that nanoparticles formed from *Ricinus communis* were more limiting with enhanced monodispersity. These particles were blended with CMC to form polymer nanocomposite. XRD showed decrease in crystallinity by addition of gold nanoparticles. FTIR confirmed the interaction of nanoparticles with the polymer which might facilitate the particles to transfer over the chain of polymer. These interactions were crucial for conduction behavior of electrolyte samples. Differential scanning calorimetry (DSC) showed that by addition of nanoparticles, thermal stability decrease and conduction enhanced in range of  $9.86 \times 10^{-12}$  to  $4.12 \times 10^{-9} \text{ S cm}^{-1}$  at 353 K.<sup>48</sup>

Abutalib *et al.*, reported the good optical, dielectric and electrical properties of CMC films grafted with polyvinyl alcohol (PVA) and graphene nanotubes. The optical energy band gap confirmed the optical characteristics of prepared polymer blends and dynamic behavior of ions of all samples were investigated by frequency dependence AC conductance. The nanocomposite films ionic conductivity increased by addition of graphene nanotubes concentration. The highest conductivity was observed  $4.53 \times 10^{-4}$  at  $30^\circ\text{C}$ .<sup>49</sup>

**2.2.6. CMC based composites as binder in Li-ion batteries.** Recently, an increase in the demand of lithium-ion batteries with improved energy density and long-lasting operation is due to their usage in portable electronic devices and large-scale batteries.<sup>50</sup> There are two major types of Li-ion batteries,

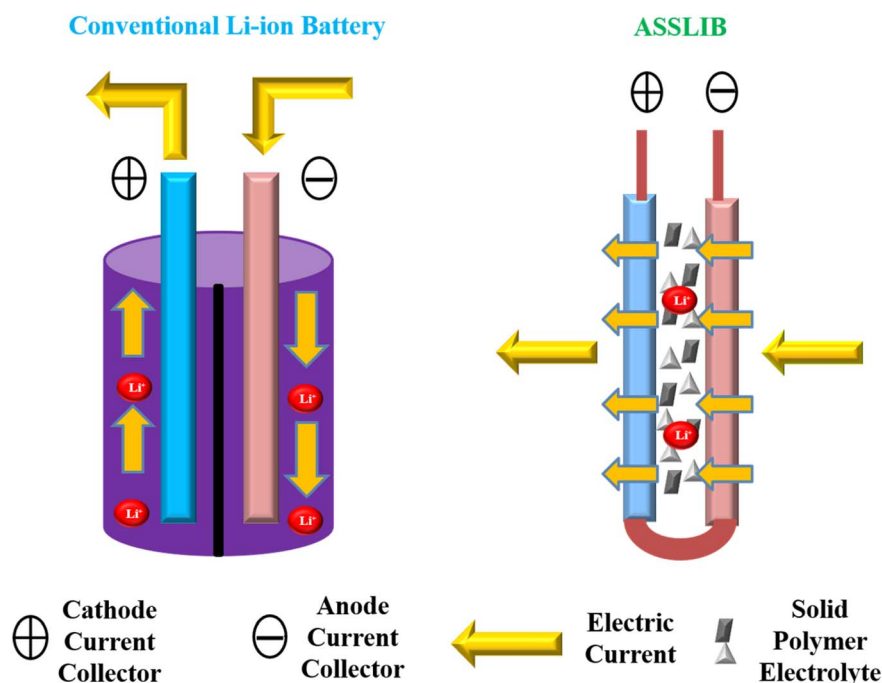


Fig. 3 A general representation of conventional and all solid-state Li-ion batteries.

conventional Li-ion batteries and ASSLIB. In a conventional battery, liquid electrolyte has been used which could be highly flammable and of high energy density.<sup>51</sup> ASSLIB has emerged as promising solution to conventional batteries because they use solid non-flammable electrolytes.<sup>52</sup> This solid electrolyte can work as separator or it can be separately present in liquid electrolyte-based batteries. Thus, ASSLIB provides safety and stability along with durable nature.<sup>53</sup> Among other binders and electrolytes, sodium carboxymethyl cellulose (Na-CMC) is a potential binder and electrolyte for solid state Li-ion batteries (Fig. 3).<sup>54</sup>

In ASSLIB, there are different ways to upsurge the energy density of the batteries two of them are: (1) by improving the specific capacity of the cell, development of the high-energy density electrodes<sup>55</sup> and (2) by improving the volumetric capacity of the cell, and designing a thick electrode with compact cell configuration.<sup>56</sup> But, the use of thicker electrode causes the enhanced diffusion of Li-ion which causes resistance to the charge transport with degradation of electrochemical performance.<sup>57</sup> Binders as major battery components, provide integrity with enhanced physiochemical properties to the electrodes (Fig. 4).<sup>58</sup> Conventional CMC based aqueous binders are reliable, low cost, environment friendly and provides high energy density to the anodes of Li-ion batteries (Table 1).<sup>59,60</sup> Yang *et al.*, reported CMC with humic as a potential binder for lithium batteries for the enhancement of electrochemical performance. Both water soluble polymers acted as combined binder for charge-discharge and cathode preparation process. The binder forms stable interface layer of cathode with significant increase in electrical conductivity of electrode. After 100 cycles, the reversible capacity was observed which was higher than cathode with traditional binder. The cathode specific capacity was 105 mA h g<sup>-1</sup> at 8 °C with discharge platform of 3.30 V.<sup>61</sup> Jeong *et al.*, reported that lithium incorporated hierarchically porous carbon monoliths (PCMs), a potential anode material in Li-ion batteries, were prepared with lithium salt of

water-soluble CMC. The porous structure of carbon and homogeneity of lithium throughout the PCMs have enhanced the electrochemical properties of composites. PCMs have low initial irreversible capacity, stable life cycle at high current density and increase in resistance at the end of the discharge. Moreover, the galvanostatic intermittent titration technique indicated the high diffusion coefficient of prepared material at the end of the discharge.<sup>62</sup> Karkar *et al.*, compared polyacrylic acid (PAA) and CMC/citric acid as binders for silicon-based negative Li-ion battery electrodes and found later one as more effective. Concentration of binder affects the electrode slurry rheology, dry electrode shape, and physical characteristics. Electrochemical behavior of electrodes is a function of active mass loading (1 to 4.5 mg cm<sup>-2</sup>). Increasing the binder concentration from 4 to 12 wt% enhances 1st cycle efficiency due to its role as a pre-formed artificial solid electrolyte inter-phase layer. Increasing the binder concentration improves the cyclability of electrodes with active mass loading over 1 mg cm<sup>-2</sup>. CMC/citric acid is more effective at low concentration and PAA at high content, perhaps due to their molecular structures. For both binders, post-processing, called maturation improves electrochemical performance.<sup>63</sup>

Cotton is also used to make the water-based CMC binder with lithium (CMC-Li). CMC-Li can enhance the lithium content, boosting the diffusion efficiency and specific capacity. The CMC-Li battery preserved 98% of its original reversible capacity after 200 cycles at 176 mA h g<sup>-1</sup>, exceeding lithium iron phosphate (LiFePO<sub>4</sub>, LFP) predicted specific capacity. The batteries are electrochemically sound, pollution-free, and stable.<sup>64</sup> Due to small loss and consistent performance, CMC-Li with high degree of substitution is preferred.<sup>65</sup> Qiu *et al.*, studied electrochemical characteristics of lithium iron phosphate and water-soluble binder cathodes, CMC-Na and CMC-Li. After 200 cycles, the CMC with lithium as binder enhanced LFP cathode cyclic ability by 96.7% at 175 mA h g<sup>-1</sup> compared to poly(vinylidene difluoride) (PVdF). The LFP electrode with CMC-

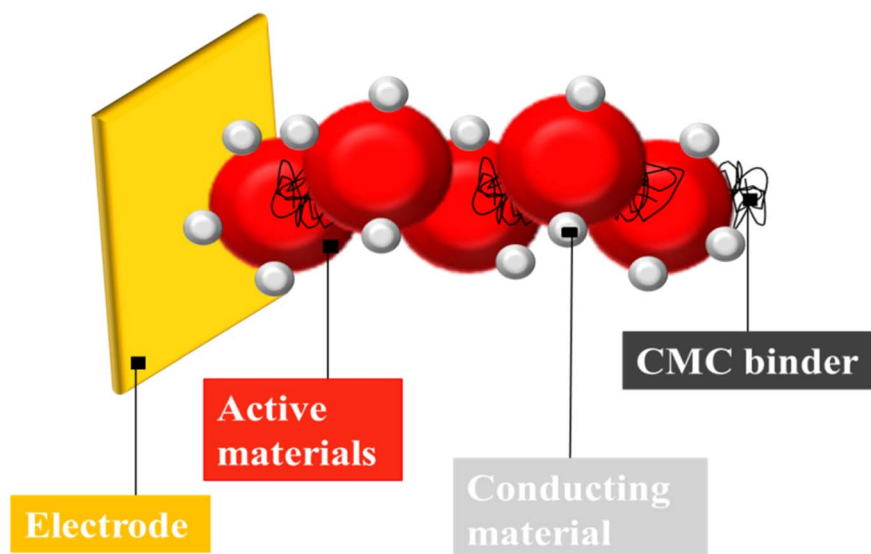


Fig. 4 A general representation of CMC as binding material in energy storage batteries.



Table 1 CMC-based materials in Li-ion batteries

CMC source	Blends/composite material	Specific capacitance (mA h g <sup>-1</sup> )	Current density (mA g <sup>-1</sup> )	Charge/discharge cycles	Applications in electrochemistry	Ref
Commercial; Sigma-Aldrich	Na-CMC/SBR as binder	450	0.2	30	• Carbon coated silicon/boron/graphite anode in Li-ion batteries	72
Commercial	Na-CMC/SBR as binder	2221		30	• Modified elastomeric binder for silicon anode in Li-ion batteries	73
Commercial	CMC as binder	149.2		200	• CMC as cheap and green binder for LiNi <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> O <sub>2</sub> (NMC) as cathode material for Li-ion batteries	74
Synthetic CMC based on cotton cellulose	CMC-Li binder	180		200	• CMC-Li is cheaper, eco-friendly, biodegradable and safer binder for Li-ion batteries' electrodes	65
Commercial; Sigma-Aldrich	Na-CMC/SBR/acrylic acid hydrogels as binder	157/162	0.5	50	• Physiochemical effect of CMC based binder for graphite anode in Li-ion batteries	71
Commercial; Sigma-Aldrich	CMC derived Li incorporated hierarchically porous carbon monoliths	312	30	50	• Pre-lithiated CMC derived porous carbon monoliths can act as an efficient material for high power anode	62

Li as the binder has the best capacity rate as compared to other binders. EIS studies demonstrate that CMC-Li has lower charge transfer resistance than CMC and PVdF alone.<sup>66</sup> CMC-Li extracted from cotton after treatment with lithium ethoxide was reported to be used as lithium-replenishing binders in the negative electrode of batteries with water as a dispersant to assemble a battery. The batteries showed better results due to reduced resistance, improved impedance, cycle period with 2500 circles and increase in life span by 20% which could be attributed to lithium supplementation. By increasing the lithium content, batteries showed improved ion conduction rate and ion conductivity.<sup>67</sup>

On one side of a pristine polyethylene battery separator, a ceramic layer composed of aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) powder, CMC, and styrene-butadiene rubber (SBR) mixed binder was effectively formed to create a coating separator made of ceramics for lithium batteries. In the preparation of separator, water as solvent was used with very little quantity of SBR-CMC combination as binder to improve the thermostability. The studies have shown that the ceramic-coated separator with SBR-CMC binder had excellent thermal stability, high fluid electrolyte absorption, and superior hydrophilicity. Tests of pouch cells with a ceramic-coated separator also demonstrate high cycle stability. The ceramic coating separator (CCS) membrane significantly improved thermal contraction, liquid electrolyte hydrophilicity, and electrolyte absorption. As the ceramic-coating layer increased on the CCS membrane, the absorption of electrolytes increased, and the thermal contraction was decreased. The pouch cells constructed with ceramic-coated separators have superior cycling performance compared to those with polyethylene separators. Because just a minimal quantity of binder is required and the solvent is water, the CCS membrane is appropriate for use in secondary lithium batteries.<sup>68</sup> Yeo *et al.*, investigated the combination of

rechargeable lithium-ion batteries with lumichrome cathodes and aqueous SBR-CMC binders. A 2S6P battery module was successfully made to power blue LEDs. Positive electrode lumichrome revealed no structural alterations compared to pristine powder. Large pouch cells had cathodic and anodic peaks with 2.58 and 2.26 V average potentials. Ethylene carbonate-dimethyl carbonate (EC-DMC) and triethylene glycol-dimethoxyethane (TEGDME) both have initial discharge capabilities of 142 mA h g<sup>-1</sup>. EC-DMC-injected pouch cells performed better than TEGDME-injected ones. This may be due to the decreased lithium-ion migration resistance at the electrode/electrolyte interphase and increased EC-DMC ionic conductivity. EC-DMC-injected pouch cells cycled more than TEGDME-injected ones. After 40 cycles, EC-DMC and TEGDME-injected cells retained 56.4% and 22.3% of their capacity. TEGDME electrolyte decomposes and swells lithium metal negative electrodes. To enhance lumichrome active materials' electrochemical characteristics, novel electrolyte systems and negative electrode materials are being studied.<sup>69</sup> Li *et al.*, reported that CMC Oxa-Michael addition with sulfobetaine methacrylate (SBMA) resulted in zwitterionic modification because zwitterion segment can simultaneously provide quaternary ammonium and sulfonic group for electron and lithium-ion receptors. The limiting molar conductivity increased (61 S cm<sup>2</sup> mol<sup>-1</sup>) and activation energy decreased (0.058 eV). This composite CMC/SBMA used as binder in graphite anode of lithium-ion batteries with discharge voltage plateau at 3.35 V and specific capacitance 140 mA h g<sup>-1</sup>. This binder had also been used in activated carbon electrode for supercapacitor with low diffusion parameter of 0.03, low internal resistance and high specific capacitance of 277.9 F g<sup>-1</sup>.<sup>70</sup> Shin *et al.*, increased the thickness of graphite anode which created a perfect cell of increased mass loading and density of the Li-ion battery. Increasing the duration of ionic migration route may reduce Li<sup>+</sup> diffusivity. Using



SBR as a binder, cross-linked poly acrylic acid–carboxymethyl cellulose hydrogels were generated to improve adhesion strength with diffusivity. Adhesion strength of electrode with electrolyte permeability were increased by 2.0 and 2.5 times, respectively, as compared to a standard CMC–SBR combination, leading to good electrochemical characteristics owing to improve interpolymeric and electrolyte properties. Retention capacity increased from 80 to 90% at 1 °C.<sup>71</sup>

**2.2.7. CMC as binder in sodium-ion batteries.** Li-ion batteries are in demand because they are used in electrical vehicles, mobile devices and electrical products.<sup>75</sup> But lithium is not an abundant metal like sodium and is expensive. Comparatively, sodium is abundant, low in cost, gaining researcher's interest to be used in sodium ion batteries. Anodes of these batteries include hard carbon,<sup>76</sup> antimony,<sup>77</sup> germanium,<sup>78</sup> tin<sup>79</sup> and tin-based materials.<sup>80</sup> But only few of them can satisfy large capacity and good cyclability. To enhance the cyclability, anodes based on alloy of various kind of binders have been used like PAA,<sup>81</sup> sodium polyacrylate,<sup>82</sup> polyimide<sup>83</sup> and CMC.<sup>84</sup> CMC binder has better discharge capacity by showing small change in electrode volume during cycling (Table 2).<sup>76</sup> For a non-aqueous sodium-ion battery, a hard-carbon negative electrode with sodium carboxymethyl cellulose (Na-CMC) binder exhibits higher repeatability and cyclability in NaPF<sub>6</sub> propylene carbonate solution at ambient temperature when compared with another binder made of poly(vinylidene difluoride) (PVdF). Moreover, the effects of the monofluoroethylene carbonate (FEC) additive rely significantly on the combination of CMC and PVdF binders. Depending on the binders and FEC additive employed for the hard-carbon negative electrodes, surface studies indicate substantial changes in surface and contact resistance chemistry. In aprotic sodium cells, the hard-carbon electrode with CMC binder exhibited more cyclability than the electrode with PVdF binder. The FEC is required as an electrolyte addition in order to enhance the cyclability of the PVdF electrode.<sup>85</sup>

Transition metal oxides were also used as electrodes for sodium-ion batteries. FeV<sub>2</sub>O<sub>5</sub> with eco-friendly and cost-

effective binders of sodium carboxymethyl cellulose/styrene butadiene rubber has proved potential anode material for batteries. The transition metal oxide worked on the principle of pseudo-capacitive process and binders showed highly stable capacity of 97 mA h g<sup>-1</sup> after 200 cycles. The higher stability might be due to the strong hydrogen bonding between carboxyl and hydroxyl groups which leads to superior binding with active material and current collector. By comparing the transition metal oxide capacitance with PVdF capacity, the later showed detachment of the electrode material from copper foil after 200 runs.<sup>86</sup> Hydrothermally produced copper oxide (CuO) nanosheets were also evaluated as anodes of sodium-ion batteries. CuO nanosheets performed well as anodes due to their unique nanosheet structure. CuO nanosheets electrode with CMC binder demonstrated much better electrochemical performance than PVdF electrode. CuO nanosheet electrodes with CMC binder exhibited 627.2 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup>. CuO nanosheet preserved 50.3% of its original capacity after 300 cycles at a current density of 2000 mA g<sup>-1</sup>. CuO nanosheets are attractive electrode materials because of their high reversible capacity, steady cycling performance, and excellent rate capability.<sup>87</sup>

**2.2.8. CMC based composites in zinc ion batteries.** Rechargeable zinc ion batteries are also a best alternative to the lithium-ion batteries in fulfilling the future energy storage demands. These batteries are of high capacity, low cost and highly abundant (Table 3).<sup>89</sup> Recently, CMC composites have been used as binder for cathodes of zinc ion batteries which keep the cathode component intact during cycling. The effect of chemical structure of the conventional and green binders on the cyclability, performance and reaction of zinc ion batteries was investigated by Jaikrajang and coworkers. They concluded that sodium ion (Na<sup>+</sup>) in CMC structure plays a crucial role in battery reaction. These batteries have high ionic diffusivity and superior cyclic stability through 500 charge–discharge galvanostatic cycles.<sup>90</sup> Similarly, Yang *et al.*, investigated the influence of CMC as additive for zinc paste electrodes in alkaline zinc batteries. They concluded that an appropriate amount of CMC in alkali can inhibit the zinc dendrite growth with

Table 2 CMC-based materials in sodium ion batteries

CMC source	Blends/composite material	Capacity (mA h g <sup>-1</sup> )	Current density (mA g <sup>-1</sup> )	Capacity retention (%)	Cycles	Application	Ref
Commercial; Daicel, Ltd	CMC/poly (vinylidene difluoride) binder	250	25	97	100	• CMC as binder for hard carbon negative electrode in sodium ion batteries	85
Commercial; Sigma-Aldrich Co. Ltd	CMC as binder	400	25		20	• Comparison of CMC binder with other kind of binders in sodium ion batteries	76
Commercial	CMC as binder	627.2	50	73.4	100	• CuO nanosheets as anode with CMC binder showed satisfactory electrochemical performance	87
Commercial	CMC/SBR as binder	97	200		200	• Spinel oxide-FeV <sub>2</sub> O <sub>4</sub> with CMC/SBR binder used as conversion-based anode material in sodium ion batteries	86
Commercial; TCI	Na-CMC as binder	635		73	60	• BiFeO <sub>3</sub> -CMC electrode in sodium ion batteries	88





Table 3 CMC based composite in zinc ion batteries

Blends/composite material	Specific capacitance (mA h g <sup>-1</sup> )	Current density (mA g <sup>-1</sup> )	Charge/discharge cycles	Ionic conductance (mS cm <sup>-2</sup> )	Applications in electrochemistry	Ref
CMC/PVA as polyelectrolyte	—	10	300	119.8	• CMC/PVA based polyelectrolyte separator in zinc iodine batteries	95
CMC/cellulose acetate	315	200	500	—	• CMC based green binders in zinc ion batteries	90
CMC and KOH as additive	—	100	—	—	• CMC as additive in zinc paste electrodes	91
Na-CMC as electrolyte	—	268.2	2800	10.08	• Na-CMC based moderately concentrated electrolyte	92
CMC/poly( <i>N</i> -isopropylacrylamide) based electrolyte	—	0.25–5	150	$1.68 \times 10^{-4}$	• Physiochemical effect of CMC based binder for graphite anode in zinc ion batteries	94

corrosion suppression.<sup>91</sup> Li *et al.*, designed CMC based electrolyte with high ionic conductivity 10.08 mS cm<sup>-1</sup> and remarkable electron density and stability (97.35% after 2800 cycles). They highlighted the feasibility of moderately concentrated electrolyte to deal with the stability issue of aqueous soluble electrode material.<sup>92</sup> Moreover, Mao *et al.*, have introduced double-network structured electrolyte based on CMC and polyacrylamide to increase the electrostatic interaction between zinc ions (Zn<sup>2+</sup>) and carbonyl groups. This interaction has remarkably increased the stability and reversibility of zinc electrode. Flexible zinc ion batteries with this electrolyte possess 90.18% capacity retention over 500 cycles at 0.31 mA cm<sup>-2</sup>.<sup>93</sup> Likewise, Dueramae *et al.*, developed CMC and poly(*N*-isopropylacrylamide) based host polymer system in SPE of zinc ion batteries. They obtained high ionic conductivity ( $1.68 \times$

$10^{-4}$  S cm<sup>-1</sup>) and greater stability during charge–discharge cyclic tests.<sup>94</sup> Tangthum *et al.*, evaluated CMC/PVA based polyelectrolyte system as cation exchange separator in zinc iodine batteries. This system has also enhanced the ionic conductance and cyclic stability.<sup>95</sup>

**2.2.9. CMC based electrodes in supercapacitors.** Electrochemical supercapacitors are observed as popular substitute of energy storage devices due to high power density, long life cycle and rapid charge and discharge rates.<sup>96,97</sup> Recently, researchers are trying to explore low cost, green electrode materials for super capacitors.<sup>98</sup> Natural polysaccharides like cellulose, starch and CMC have been considered promising candidates for electrode materials (Table 4).<sup>99</sup> CMC has cellulose backbone, rich in oxygen content due to carbonyl and hydroxyl groups, provides rich carbon source for oxygen self-doping in electrode

Table 4 CMC-based materials in supercapacitors

CMC source	Blends/composite material	Specific capacitance (F g <sup>-1</sup> )	Current density (A g <sup>-1</sup> )	Cycles	Voltage (V)	Applications in electrochemistry	Ref
Commercial; Tianjing Yuanli Chemical Co., China	Sodium carboxymethyl cellulose (Na-CMC)/ polyaniline nanorods	425.25	1	1000	−0.2 to 0.8	• CMC/polyaniline nanorods are used in high performance redox supercapacitors	116
Commercial; Anli (Henan, China)	Na-CMC aerogels	152.6	0.5		−0.1 to 0 in 6 M KOH solution	• Na-CMC aerogel enhanced electrochemical performance supercapacitors	110
Commercial; Zhiyuan Chemical Reagent Co., Ltd	CMC/bacterial cellulose/ citric acid based hierarchical composite porous carbon	350	0.5	10 000		• Renewable biomass-derived carbon material and its application in supercapacitors	103
Commercial	CMC based polypyrrole–vanadium oxide composite on graphite electrode in acetonitrile	800	5.3	1000	1 mA cm <sup>-2</sup>	• CMC based composite applications in asymmetric supercapacitors	39
Commercial; Anli LLC (Henan, China)	Na-CMC derived nitrogen doped carbon aerogels	185.3	0.5	5000	−1 to 0	• Na-CMC derived aerogels can be used as electrodes in supercapacitors	101
Commercial; Sigma-Aldrich	Porous carbon pearls of CMC	217	1	10 000 at 30 A g <sup>-1</sup>	0 to 1	• Porous CMC derived pearls as active material for double-layer capacitors	108



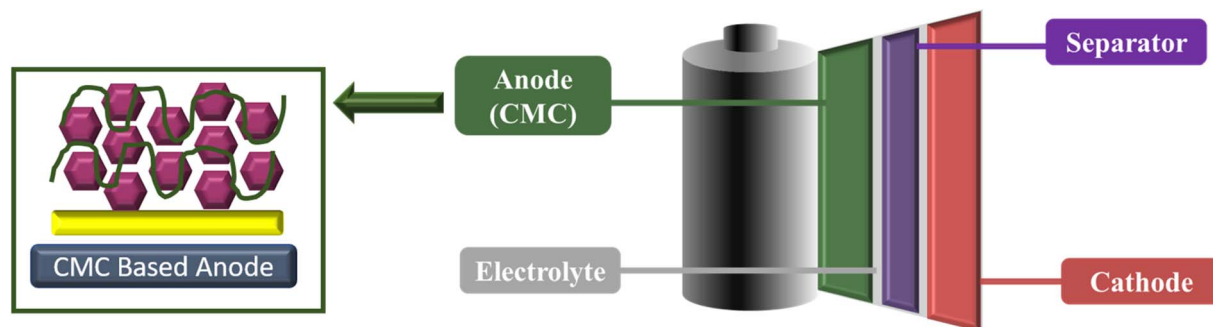


Fig. 5 A simple representation of CMC based electrode as anode in the battery of supercapacitors.

materials (Fig. 5).<sup>100</sup> For example, polypyrrole/sodium carboxymethyl cellulose (PPy/CMC) nanospheres were produced by *in situ* oxidative polymerization of pyrrole with CMC as a polymerization template. The composite's size and shape were homogenous, with a diameter of around 100 nm. After adding CMC as a template, the hybrid electrode exhibited high cyclic stability, with 80% retention after 200 charge and discharge cycles.<sup>35</sup>

CMC based carbon aerogels with nitrogen doping also exhibit the potential to be utilized as electrode in supercapacitors. These were prepared *via* multistep advanced approach comprising sol-gel, freeze drying, carbonization and base stimulation process with ferric trichloride ( $\text{FeCl}_3$ ), collagen as cross-linker and nitrogen source. These carbon aerogels showed porous, three dimensional and higher surface area with magnetic properties. As an electrode material, the aerogel displayed current density  $0.5 \text{ A g}^{-1}$  and specific capacitance  $185.3 \text{ F g}^{-1}$  in a 6 M KOH electrolyte. The retention of specific capacitance was 90.2% after charge and discharge cycle showing cycling stability.<sup>101</sup>

CMC intercalated reduced graphene oxide films are also gaining considerable attention in charge storage devices due to their flexible, wearable and bendable nature. Reduced graphene oxide usage is challenging due to its density stacked structure with poor wettability to the electrolyte. Addition of CMC in reduced graphene oxide has acted as activating agent. The composite films were reduced to improve the electrochemical properties due to the increase in assessable area for electrolytic ions. The polymer composite films showed drastic increase in capacitance after charging/discharging cycles owing to electro activation and pseudo capacitance as compared to reduced graphene oxide film alone.<sup>102</sup> Shu *et al.*, have employed hierarchical porous carbon materials prepared from composite material of CMC/bacterial cellulose/citric acid as an electrode in supercapacitors. The prepared material has excellent rate capability of  $254 \text{ F g}^{-1}$  at current density  $15 \text{ A g}^{-1}$ , 96% capacitance retention of cyclic stability after 10 000 cycles tests with enhanced rate capability and high specific capacitance of  $350 \text{ F g}^{-1}$  with current density at  $0.5 \text{ A g}^{-1}$ . In aqueous KOH electrolyte, the symmetric porous carbon electrode showed higher specific capacitance and electron density of  $28 \text{ W h kg}^{-1}$ .<sup>103</sup>

Ali *et al.*, have employed bidirectional approach by using CMC samples from two different sources, bamboo (BCMC) and

oil palm empty fruit bunch (OCMC), prepared by simple incipient wetness impregnation method proceeded by calcination process and incorporation of manganese oxide ( $\text{Mn}_2\text{O}_3$ ). The carbonization step has converted CMC into porous CMC and surface area in case of BCMC was more than OCMC. After incorporation of metal oxide, the crystalline size of both CMC has reduced. Comparatively, BCMC/ $\text{Mn}_2\text{O}_3$  composite film comprised of higher electrochemical performance ( $31.98 \text{ mF cm}^{-2}$ ) than OCMC/ $\text{Mn}_2\text{O}_3$  ( $24.15 \text{ mF cm}^{-2}$ ). However, both CMC showed fairly high cyclic stability after 1000 charge/discharge cycles.<sup>104</sup>

An antifouling nanohybrid membrane comprising of CMC, graphene oxide nanosheet and magnesium oxide ( $\text{MgO}$ ) nanoparticles was synthesized for water treatment and as an electrode in supercapacitor applications. TEIS Nyquist plots revealed the supercapacitor and energy applications of hybrid material.<sup>105</sup> After that, another hybrid nanomaterial containing yttrium oxide ( $\text{Y}_2\text{O}_3$ ) with modified graphene oxide and CMC has been prepared to utilize it as electrode in supercapacitor. The electrochemical properties were inspected by CV, Tafel plot and EIS which showed nanomaterial as promising candidate for energy storage and supercapacitors applications.<sup>106</sup>

CMC based macrostructure in combination with graphene oxide showed the potential to be used as antifouling membrane for pollutant detection and as an electrode in supercapacitor applications. Impedance analysis of fabricated nanocomposite approved the movement of charges between electrolyte and electrode for the accomplishment of specific capacitance.<sup>107</sup>

$\text{BiFeO}_3$ -CMC electrode has excellent electrochemical performance in combination with fluoroethylene carbonate (FEC) as electrolytes. These electrodes delivered initial capacity values of 635 and  $453 \text{ mA h g}^{-1}$  in charge/discharge process in the electrolyte composition of 1 M  $\text{NaPF}_6$  in EC/DEC (1 : 1, v/v) with 2% FEC additive. The capacity retention of 73% with capacity value stabilized around 10th cycle after 60 cycles.<sup>88</sup> Chang *et al.*, have developed porous carbon pearls (PCPs) from concentrated solution of CMC followed by ice-templating and carbonization. The PCPs with pearly luster had well developed bi-model pore structure with total pore volume of  $0.81 \text{ cm}^3 \text{ g}^{-1}$ , specific surface area  $1338.6 \text{ m}^2 \text{ g}^{-1}$ . The PCPs electrode showed high supercapacitive performance in three-electrode system with maximum specific capacitance of  $217 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  in aqueous KOH electrolyte, excellent cyclic stability (100%) after



10 000 cycles at  $30 \text{ A g}^{-1}$ . To infer concrete super-capacitive potential, a symmetric capacitor device was equipped by utilizing a coin cell which showed specific capacitance of  $37 \text{ F g}^{-1}$ , power density of  $5.0 \text{ kW kg}^{-1}$ , energy density of  $2.88 \text{ W h kg}^{-1}$  and current density of  $1 \text{ A g}^{-1}$ . Moreover, this device had superior capacitance retention 98.5% and cycling stability of 10 000 cycles at current density of  $10 \text{ A g}^{-1}$ .<sup>108</sup>

**2.2.10. CMC aerogels pyrolyzation for the production of carbon aerogels (CAs).** Pyrolysis of CMC aerogels with potassium hydroxide (KOH) activation produces porous carbon aerogels. Activation affects the characteristics of carbon aerogels. After 3 hours of KOH activation, carbon aerogels had  $428 \text{ m}^2 \text{ g}^{-1}$  specific surface area (SSA).<sup>109</sup> Due to its extremely porous and linked 3D nanostructures, activated carbon aerogel boosted supercapacitor electrochemical performance. Specific capacitance achieved  $152.6 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$  in KOH solution (6 M) between 1.0 and 0 V. As-prepared carbon aerogels absorbed  $249.6 \text{ mg g}^{-1}$  methylene blue and  $245.3 \text{ mg g}^{-1}$  malachite green. These carbon aerogels are a potential material for energy storage, catalysis, and sewage treatment due to their increased electrochemical performance and dye adsorption capabilities.<sup>110</sup> Méndez-Morales *et al.*, have prepared loaded thick electrode with the highest mass that is a possible structural solution for enhancing supercapacitor energy density. However, the slowest ion transport with sluggish charge kinetics generated by the improved electrode thickness continue to pose significant obstacles to the advancement of high-performance energy storage systems.<sup>111</sup> The fabrication of cellulose carbon aerogel-based separator, anode and cathode provides a one in all biopolymer aerogel based asymmetric supercapacitor device (Fig. 6). Both cellulose and carbon aerogel, by virtue of their three dimensional hierarchical porous percolation network structure, provide electrolyte penetration-friendly continuous

routes, hence enabling the fast movement of ions and electrons.<sup>112</sup>

Sodium salt CMC as a carbon source and nickel sulfate as a nickel precursor, were treated by a sol-gel procedure, freeze-drying, and pyrolysis.<sup>113</sup> The prepared carbon aerogel (CA)/NiO composites have a three-dimensional network structure, broad surface area, and outstanding magnetic characteristics. NiSO<sub>4</sub> affects composites' electrochemical characteristics.<sup>114</sup> The CA-1.0 composites demonstrate better specific capacity ( $81.67 \text{ mA h g}^{-1}$  at  $0.5 \text{ A g}^{-1}$ ) in KOH electrolyte solution (6 M), based on the coupling of CA double-layer capacitance and NiO redox reaction. After 5000 charge-discharge cycles, the CA-1.0 electrode retains 94.5% of its capability. A simple and affordable approach for making carbon/NiO composites has excellent possibilities for enhanced energy storage systems.<sup>115</sup>

### 3. Applications of CMC in energy conversion and generation devices

The efficiency of energy conversion is a central parameter for optimization and development of power generation devices.<sup>117</sup> Recently, CMC has gained importance as an active material in energy conversion devices such as fuel cells and triboelectric nanogenerator (TENG) which are listed below.

#### 3.1. CMC in fuel cells

Microbial fuel cell is the device that can convert chemical energy stored in organic matter into the electrical energy by utilizing microorganisms as anode catalyst.<sup>118</sup> These cells are considered environment friendly, highly efficient, superiorly performing and new for the growth in green energy.<sup>119,120</sup> But their practical applications still face problems like lack of energy storage and low power generation.<sup>121,122</sup> Anodes are

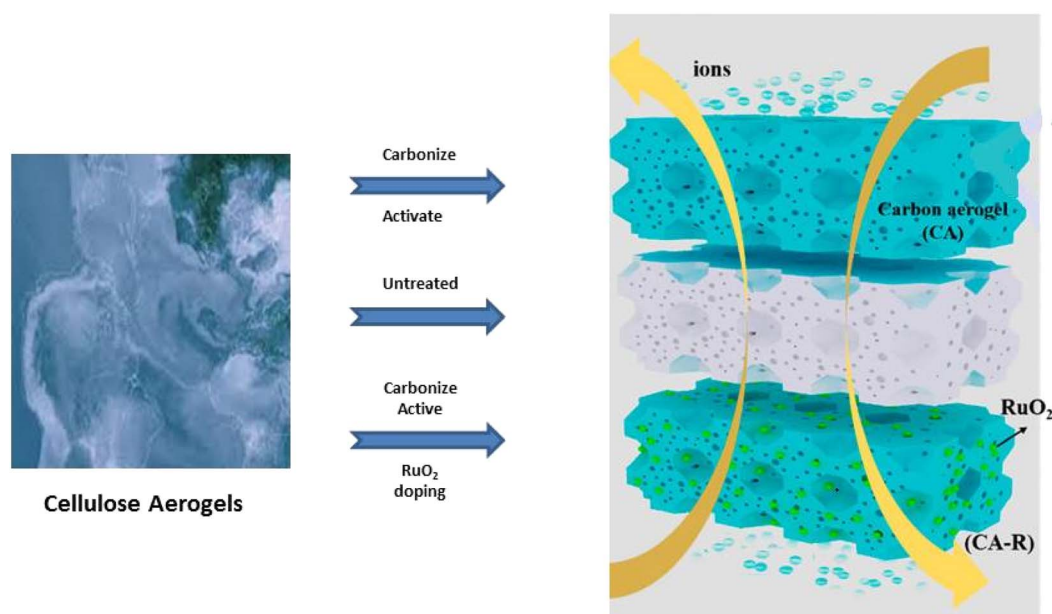


Fig. 6 A simple representation of activating relation between cellulose and carbon aerogels in the presence of metal oxide.

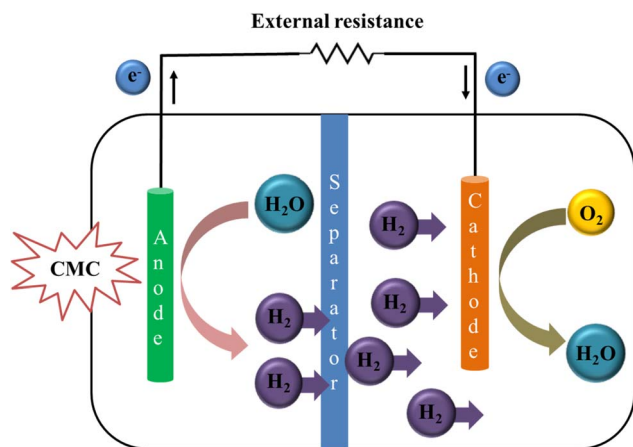


Fig. 7 A graphical representation of CMC based materials as anode in microbial fuel cells.

crucial for these cells as they are main thing in current output and affecting power.<sup>123,124</sup> Anode material must be promising for electricity producing bacteria and conductivity.<sup>125,126</sup> Conducting polymers due to their high conductivity and redox behavior have received great attention in this field. CMC based conducting materials are already used in electrochemistry and biosensors (Fig. 7).<sup>126</sup> As CMC forms a transparent adhesive liquid after swelling in water, so CMC is highly effective as water-based binder.<sup>85</sup> Small quantity of unreacted CMC in composites is effective for the binding of substrate with composite material which is also good for electrode stability.<sup>127</sup> Wang *et al.*, studied microbial fuel cells which utilize wastewater stored chemical energy and modified them by alteration of anode with ternary composite hydrogel of CMC/polypyrrole/titanium nitride/carbon brush hydrogel. This bioanode has enhanced the energy output of microbial fuel cell. SEM analysis confirmed the three-dimensional macroporous structure with enlarged area on surface for the growth of microorganisms. The energy density ( $14.11 \text{ W m}^{-3}$ ) and current density of ternary hybrid anode were 4.72 and 10.12 times larger than blank carbon brush anode. The synergistic effect of polymers has improved the potential of electrochemical anode.<sup>128</sup> A single medium sediment microbial fuel cells (SMFC) differs from traditional SMFC in that the cathode is immersed in an anoxic sediment environment to prevent oxygen from competing for electrons and to improve the likelihood of electron acceptors copper ions reduction. The sediment containing higher copper ions restricts microbial growth, necessitating the development of a viable solution to this issue. The copper tolerant bacteria immobilized on carboxymethyl cellulose (CMC) beads serve variety of purposes, such as the adsorption of copper ions, defense against inhibition by large levels of copper ions, and enhancement of copper tolerant bacteria activities as co-substrate. The results demonstrate increased organic removal (85%) by copper tolerant *Ochrobactrum oryzae* at high copper ion concentrations, which was 1.48–1.65 times and 5 times more efficient than those comprising other strains and blended bacteria. *Ochrobactrum oryzae*'s inhibition by copper in the

sediment was lessened as a result of the immobilization of the organism with CMC, which also assured the SMFC's ability to generate electricity steadily. The highest output voltage (173.9 mV) and copper ion removal rate (>70%) attained with the addition of cell-immobilized beads to the SMFC anode zone were 2.89 and 1.15 times greater than those values without the beads, accordingly. On 70th day, electrochemically active species of bacteria that could break down organic molecules dominated the anode zone.<sup>129</sup>

### 3.2. CMC in triboelectric nanogenerator (TENG)

TENG is a green energy conversion device which can convert low quality and low frequency mechanical energy into low current and high voltage electric energy.<sup>130</sup> It works on the principle of contact electrification and electrostatic induction coupling.<sup>131</sup> TENG is composed of three components; negative layer, positive layer and conductive electrodes.<sup>132</sup> Recently, CMC based materials have been used in negative and positive layers of TENG and provide a new idea for environment friendly TENG. Jaiban *et al.*, developed cellulose extracted from soybean and its CMC based biofilm as negative part of triboelectric generator (TENG) with maximum voltage of 28 V and current of 80 nA. This designed system had the capacity to lit up three commercial LEDs.<sup>133</sup> Similarly, Qu *et al.*, used CMC, epichlorohydrin and polyethyleneimine (PEI) based aerogel as positive layer material of TENG. The corresponding aerogel and TENG produced voltage of 203 V and current density of  $8.2 \mu\text{A cm}^{-2}$ . The tribopositive performance of CMC was increased by physical mixing with PEI (Fig. 8). This developed open circuit voltage and current can reach 385 V and 51  $\mu\text{A}$ , respectively.<sup>134</sup>

Recently, a very interesting application of TENG has been reported by Kang *et al.* The babies who like to bite, TENG has come to their rescue. The prepared TENG based on Na-CMC and carboxymethyl chitosan dissolves quickly in aqueous environment without any side effects. It has excellent electric performance with output power of  $120 \text{ mW m}^{-2}$ .<sup>135</sup> Likewise, Ya *et al.*, studied the MXene/CMC based TENG for mechanical energy harvest. This TENG exhibits the power density of  $402.94 \text{ mW m}^{-2}$  with external resistance 18 M $\Omega$ . Moreover, this TENG has bright potential to harvest energy and can protect the humans from electromagnetic radiations.<sup>136</sup>

## 4. Applications of CMC in electrical devices

In flexible electronics, CMC has been used as carbonized CMC and acts as smart fabric for manufacturing of devices.<sup>137</sup> In electrical actuators and biosensors, CMC based hybrids can sense biogenic molecules and external stimuli (Table 5). Moreover, CMC has range of applications in biogel ion electrical actuators as listed below.

### 4.1. CMC based blends as biosensor

CMC or CMC-based hybrid materials have been effectively used to sense biogenic compounds in the humans and other living organisms. In 2004, Wu *et al.* designed a glucose biosensor to





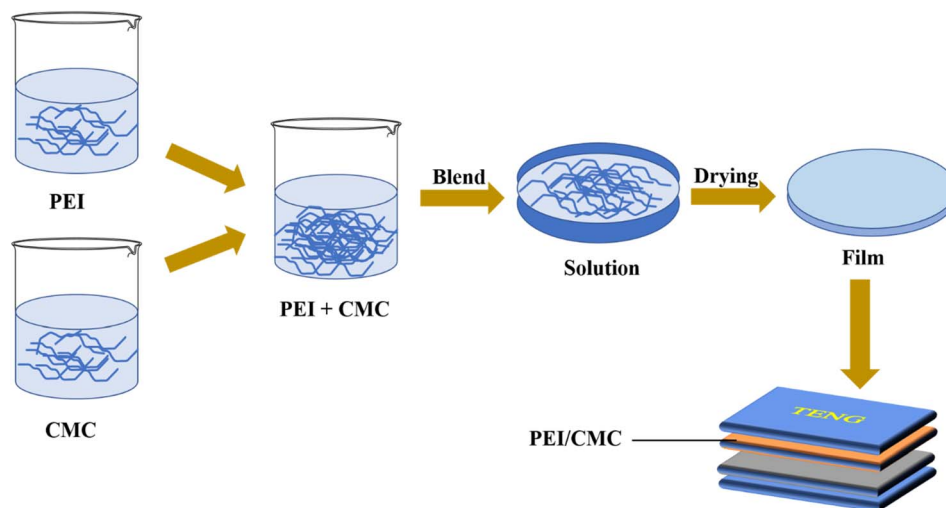


Fig. 8 A schematic representation of CMC and PEI based biofilm development for TENG layer.

entrap an enzyme, glucose oxidase, into xerogel matrix of hydroxyethyl CMC polymer and tetraethyl-orthosilicate. This fabricated sensor exhibited excellent analytical ability to detect glucose in urine samples.<sup>138</sup> After that, CMC based materials have been in fashion as sensors for detecting biomolecules (amino acids, neurotransmitters, proteins), pollutants, micro-organisms and body fluids. Applications of CMC as biosensors for  $\text{H}_2\text{O}_2$  and some biomolecules are summarized in succeeding sections.

**4.1.1. Detection of  $\text{H}_2\text{O}_2$  in biological systems via CMC based sensors.** Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is present throughout the body; it contains highly reactive oxygen specie, and plays various roles in psychological processes such as immune activation, cell signalling and apoptosis.<sup>139,140</sup> The exceeding limit of  $\text{H}_2\text{O}_2$  is detrimental to health causing cancer, inflammatory disease and cell damage. It is difficult to detect its concentration in the body due to high reactivity and low physiological concentration, that is why, researchers are developing sensors to quantify and detect its presence in biological system and CMC is playing an active role in its detection.<sup>141</sup> For example, Medrikova *et al.*, investigated that CMC stabilized iron oxide

nanoparticles have the capacity to absorb the metal ions on their surface which is effective for biosensor fabrication. Metal ions were trapped by magnetic surface of CMC and reduced without the support of any other reducing agent. These nanocomposites have high saturation magnetization ( $68.4 \text{ emu g}^{-1}$ ) and could easily be collected and separated by the influence of external magnetic field. Both metal composites possessed high reusability in catalytic reduction of 4-nitrophenol in the presence of sodium borohydride and cathodic reduction of  $\text{H}_2\text{O}_2$ . They also determine the enhancement factors of Raman signal of rhodamine 6G which were  $2 \times 10^7$  and  $3.2 \times 10^7$  in gold and silver cases, respectively.<sup>142</sup> Althomali *et al.*, developed a novel nanohybrid biosensor material-based polyaniline, dialdehyde CMC and zinc oxide (ZnO) to detect the hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the environment. Different approaches like CV and differential pulse voltammetry (DPV) were used to observe the reduction of  $\text{H}_2\text{O}_2$ . For suitable determination of  $\text{H}_2\text{O}_2$ , highly conductive platform based on nanocomposite electrode was created which indicated a good linear range and low detection limit of 0.45 M for  $\text{H}_2\text{O}_2$  determination under optimal pH 5.7. The DPV showed direct increase with peroxide concentration.

Table 5 CMC composites as biosensors

Material	pH	Electrochemical at method	Linear range	Limit of detection	Chemical detection	Ref
Multiwalled carbon nanotube/hydroxypropyl- $\beta$ -cyclodextrin functionalized CMC	5.7	DPV, CV, EIS	500–9000 $\mu\text{M}$	1.9 $\mu\text{M}$	Tryptophan	145
Polyaniline/multiwalled carbon nanotubes/CMC	7	CV	0.05–5 mM	0.01 mM	Ascorbic acid	144
Carbon nanotube/CMC		CV			Catecholamines	149
Reduced graphene oxide/CMC	7.4	EIS	0.5–10.0 $\mu\text{g mL}^{-1}$	61 $\text{ng mL}^{-1}$	Adiponectin	150
Oxidized-CMC-sulfate/sulfated polyaniline composite	5.7	DPV, CV, EIS		0.05 $\mu\text{M}$	Nitro-phenol	148
Hybrid PANI@dialdehyde CMC/ZnO nanocomposite	5.7	DPV	0.50 to 5 $\mu\text{M}$	0.45 M	$\text{H}_2\text{O}_2$	151



The linear value of concentration was in the ranges of 0.5–5 and 10–50  $\mu\text{M}$ .<sup>143</sup>

#### 4.1.2. CMC based sensors for detection of biomolecules.

CMC based sensors are effective for detection of various bodily molecules whose increasing and decreasing concentration can cause serious health problems such as amino acids, proteins, enzymes and acids. An example is the integrated ternary green-nanocomposite material based on polyaniline, multi-walled carbon nanotubes and carboxyethyl cellulose. The prepared composite material has shown well-adjusted hydrophobic and hydrophilic characters, higher stability and surface area, improved electrochemical properties with integrated compact granular morphology when compared with pristine polyaniline and binary system. The size, pore volume, pore size and average surface area were 50 nm, 0.06  $\text{cm}^3 \text{g}^{-1}$ , 14 Å and 169  $\text{m}^2 \text{g}^{-1}$ , respectively. The composite was utilized to detect model analyte, ascorbic acid, electrochemically. The carbon electrode possesses good sensor response with linear range 0.05  $\text{mM}^{-5}$  mM, limit of detection 0.01 mM and sensitivity 100  $\mu\text{A mM}^{-1} \text{cm}^{-2}$ . The composite could be dispersed in water due to CMC hydrogel solubility, proved to be good entrant for conductive ink formation and electrochemical membrane application.<sup>144</sup>

Ji *et al.*, have performed an interesting work by examining electrochemical chiral recognition of tryptophan (trp) enantiomer based on biosensor developed by grafting CMC with hydroxypropyl- $\beta$ -cyclodextrin, multi-walled carbon nanotubes and copper ions on the external surface of glassy carbon electrodes. The DPV showed oxidation peak current ratio reached at 2.2 under optimal experimental conditions. The highest electrochemical signal was observed with L-trp due to its stronger affinity than D-trp. The as-prepared biosensor also showed significant utilization for the detection of D-trp in the racemic mixture.<sup>145</sup> CMC based carbon nanotube electrode has been used in the detection of neurotransmitter catecholamines which exhibits electron transfer chemical reaction. The catecholamines electrochemical affinity based on kinetic property of intramolecular cyclization rate of chemical reaction. The apparent ECE profile in CV of composite electrode was justified by DigiElch simulation program. The cyclic voltammetry (CV) results verified the electrochemical performance of catecholamines due to cyclization which involves hydrogen ions with pH effect.<sup>146</sup> A new electrochemical immunosensor for the detection of the adiponectin cytokine was developed using a reduced graphene oxide-carboxymethyl cellulose hybrid (CMC-rGO). Covalent bonding of oxidized CMC to GO layers was followed by chemical reduction using sodium borohydride ( $\text{NaBH}_4$ ) to produce the hybrid material. Anti-APN capture antibody was immobilized in a sandwich-type immunoassay using the commercial metal-complex-based polymer Mix&Go™. HRP-Strept and Biotin-APN were employed in the assay design. Comparing findings from ELISA kits with the developed immunosensor showed that the 61  $\text{ng mL}^{-1}$  detection limit and excellent storage stability were adequate for the measurement of the target analyte in human serum. It's worth noticing that the immunosensor has a major advantage over the ELISA kit in terms of the overall assay time. The ELISA kit may be used in as

little as 2 hour after the antibody has been immobilized, however the total duration is close to 5 hours.<sup>147</sup> The role of deposition of oxidized-sulfated-CMC and sulfated polyamide on glassy carbon electrode were investigated by Alamry *et al.*, in non-enzymatic, mediator free electrochemical sensing of *ortho*-nitrophenol in orange juice samples, milk and water. Electrochemical characterizations were confirmed through CV, EIS and DPV. The functional groups on modified CMC like  $-\text{OH}$ ,  $-\text{SO}_3$  and  $-\text{COOH}$  were excellent for polymerization and adsorption of 2-NP. Under optimal concentration 2-NP showed linear correlation and low detection limit of 0.05  $\mu\text{M}$  was observed.<sup>148</sup>

#### 4.2. CMC in electrical actuators

In this era, biogel based actuators<sup>152</sup> are considered darling of scholar due to their smartness. They are driving force for robots and intelligent mechanical system,<sup>153</sup> can sense the external stimuli<sup>154</sup> like temperature, magnetic field, voltage with generation of expansion, reversible contraction and rotation.<sup>155,156</sup> Recently, they have become research focus in the field of bionics due to their properties which are as same as biological muscle<sup>157</sup> such as low weight, low energy consumption, flexible movement, no noise, small driving voltage and large deflection displacement.<sup>156,158</sup> Lv *et al.*, investigated a biogel ion electrical actuator that was prepared by using raw materials, sodium alginate (SCIA sample) and CMC. The influence of sodium alginate and CMC ratios on deflection displacement and output force was investigated which proved that optimal mass 0.25 g of CMC was helpful in improving the response speed of 0.176  $\text{mm s}^{-1}$ , deflection displacement of 17.137 mm and output force of 2.675 mN. The maximum output force density 15.970  $\text{mN g}^{-1}$  and specific capacitance 96.95  $\text{mF g}^{-1}$  were improved as compared to carboxymethyl chitosan and sodium alginate cross linking reaction. When ratios of both polymers increased, the output force displacement and deflection displacement declined due to excessive cross linking which caused blockage of three-dimensional network structure and ion channel decreased, resulting in degradation. Infrared indicated that combination of both polymers has resulted in macromolecular chain structure which enhanced the electrostatic effect due to the attraction of internal charge of the molecule. Addition of glycerin had improved the flexibility, expansion of ion channels and increase in deflection amplitude. The water preservation in the SCIA sample was helpful in the increase of working life of biogel ion actuator.<sup>159</sup> Again, this group studied biogel based actuators as new smart materials. Chitosan properties enhanced by crosslinking with CMC and tannic acid through freezing technology were employed to design novel actuators. The freezing treatment enhanced the elastic modulus, specific capacitance and output force by 0.014 MPa, 1.590  $\text{F g}^{-1}$  and 5.943 mN than the unfrozen treated samples. FTIR showed the interaction of sample after freezing treatment, SEM indicated a channel type macroporous structure due to fine distribution of water molecules.<sup>160</sup> Wei *et al.*, proposed to fabricate the actuating material that can meet the balance between mechanical integrity (specifically tensile strength) and humidity response for generators, soft robotics, artificial muscles and



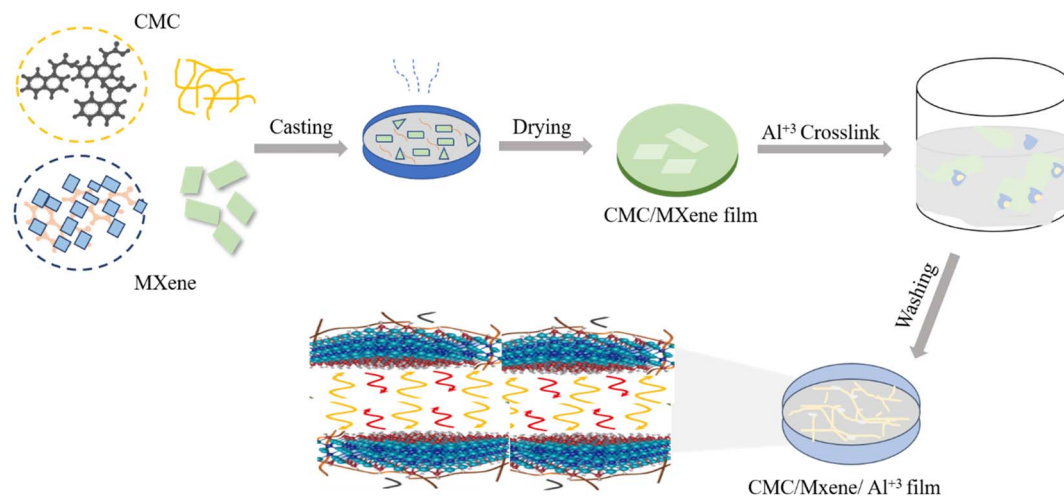


Fig. 9 A graphic representation of CMC and MXene based film for the development of sensitive actuator.

biomimetic devices. They employed a simple evaporation-induced self-assembly strategy to create a durable yet extremely sensitive merged film-based humidity actuator by utilizing biopolymer CMC, aluminum ions ( $\text{Al}^{3+}$ ) and MXene nanosheets. The closely packed hierarchical microstructure, in combination with hydrogen and ionic bonding with the complementary reinforcement effects of MXene nanosheets and  $\text{Al}^{3+}$ , results in a remarkable tensile strength of 154.2 MPa at >95% humidity, as well as strong mechanical properties of 273.6 MPa and preferable toughness of  $7.95 \text{ MJ m}^{-3}$  (Fig. 9). Interestingly, when exposed to humidity gradients, the composite film exhibits substantial shape deformation, sensitive actuation (less than 2.3 s), and outstanding cycling stability (above 1500 cycles) attributed to the exceptional lamination structure and water induced swelling action of biopolymer. Owing to the aforementioned advantages, the composite film actuator can be effectively built to fabricate smart materials like artificial muscle, human finger and moist electrical generator.<sup>161</sup>

## 5. Conclusion and future outlook

In rapidly growing field of electrochemistry, the aqueous processing of solid electrolytes, binders and electrodes is still much unexplored field. One of the water-soluble polymers is CMC, which has certain desirable attributes that perfectly fit it for application in electrochemical devices. Its characteristics to form hydrogen bonds with other polymers and swelling in water to form thick paste are giving it an edge over other synthetic polymers. Thus, CMC can be turned into a conducting material *via* modifying it with certain biopolymers and active functional groups that make it suitable for energy storage appliances. From past many years, potential of modified CMC has been explored as a conducting material in electrolytes, binder in electrodes of storage cells, active material in fuel cells, TENG and electrical actuators as discussed in this review. This developing work on electrochemical potential of CMC has made us to anticipate for its full exploitation in storage cells and electricity

devices. Future researchers must focus to explore the following aspects:

- (1) Bio-sourced polymers must be preferred over synthetic polymers to lower the cost and enhance the lifetime of batteries.
- (2) CMC composites as activating materials in fuel cells, TENG and actuators is less investigated, there must be substantial progress in these fields.
- (3) In order to fully access the applications of CMC based materials, the process must be validated on large scale.

## Conflicts of interest

Authors declare no conflict of interest.

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