

Current status and challenges of biohydrogels for applications as supercapacitors and secondary batteries

Elaine Armelin,^{a,b*} María del Mar Pérez-Madrugal,^{a,b} Carlos Alemán^{a,b} and David Díaz Díaz^{c,d*}

Progress in the chemical sciences has formed the world we live in, both on a macroscopic and on a nanoscopic scale. The last decade witnessed the development of high performance materials that store charge on many ways, from solar cells to fuel cells, from batteries to supercapacitors devices. One could argue that inorganic hybrid materials have played a central, starring role for the assemble of various electrochemical energy conversion systems. However, energy conversion systems fabricated from biopolymers has just emerged as new prospect. Here we summarize the main research results on the attractive use of biohydrogels for the fabrication of either conductive electrolytes or electrodes for battery science and technology.

1. Introduction

Nature offers abundance of examples of polymeric biomolecules from the aspects of both simplicity and complexity. Biopolymers are naturally occurring materials that have aroused a tremendous interest for their application to useful engineered technical systems. As a matter of fact, biopolymers obtaining and processing are the key steps of product-form finishing development, which are the essence of all known current applications. However, basic strategies followed to reach such steps are not related with biology but more specifically with polymer chemistry and physics. Essentially, three core aspects need to be explored for this purpose: (i) to elucidate of structure–function relationships from the study of biomimetic model systems and to apply them to easily scale-up fabrication processes; (ii) to correlate ordered primary structures with the properties required for further engineering applications; and (iii) to discover new pathways for biopolymer processing, which are expected to extend the scope of the natural system to design and develop new materials.

In fact, new approaches are almost solving all questions. Soft materials, like hydrogels, exhibit a number of unique properties. Among those properties, multifunctionality, biocompatibility, adaptability and responsiveness to stimuli, and tuneable [or tunable, American english] strength and elastic modulus deserve special attention.¹ Hydrogels are not only model systems suitable for investigating natural phenomena, such as shape transformation, but also very promising components of hybrid materials that can acquire a pre-programmed shape and electroconductive properties for electrode and electrolyte production.

Such soft materials have been extensively explored and are widely used in diverse biomedical applications, as for example tissue engineering,^{2,3} drug delivery^{4,6} and molecular actuators.^{7–9} Furthermore, their applicability has been extended to self-healing^{10,11} and soft robotics.¹² In addition, they have new and ongoing recent applications in electronic devices, like fuel cells, optoelectronic devices,¹³ organic batteries and supercapacitors.^{14–17} Indeed, they can be scaled-up using sustainable processes (*i.e.* using non-toxic solvent and low or moderate temperatures) based on

their ability to be deposited as a liquid, enhancing production viability.

Regarding sustainable processes, Billiet *et al.*¹⁸ produced 3D gels, based on gelatin methacrylamide activated with photoinitiators, which were printed laden with HepG2 cells using a 3D-bioplotter. 3D printing has grown in sophistication since the late 1970s, otherwise 4D printing is the next revolution fabrication process that converts the 3D shape to another ordered shape. The 4D dimension can be activated by time-, temperature-, mechanical- or water-stimulation; as that happens with hydrogel when it absorbs water. Recently, Spinks and co-workers¹⁹ fabricated a smart valve by 4D printing of thermally actuating and mechanically robust hydrogels. These 4D structures, which involved an interpenetrating network of alginate and poly(*N*-isopropylacrylamide), were obtained by printing that “dynamic” hydrogel ink alongside other static materials. The result is a smart hydrogel actuator able to control the water flow dependent on the water temperature. Both methods, 3D and 4D, can be scaled-up for the preparation of supercapacitors and batteries based on biopolymer hydrogels (also called biohydrogels).

Supercapacitors (SCs), also called ultracapacitors, are electrochemical energy storage devices capable of providing higher power density and longer cycling life compared to batteries. Supercapacitors are formed by two non-reactive porous electrodes, which are immersed in an electrolytic medium and electrically isolated by a membrane that is porous enough to enable the migration of ions (Figure 1A). According to differences in the charge storage mechanism, SCs can be categorized into two families: electrical double layer capacitors (EDLCs) and redox capacitors. Both types present an interface (electrical double layer) between an electronic conductor and an ionic conductor, an electrolyte.¹⁶

In a battery one or more electrochemical cells are electrically connected to supply energy. Depending on the energy consumption, batteries can be classified into two families. Primary batteries are intended to be used until exhausted and then discarded. Accordingly, discharge is the primary process during operation of such batteries, which are assembled in the charged state. In contrast, secondary batteries (also named rechargeable

^a Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya, Avda. Diagonal 647, E-08028, Barcelona, Spain.

^b Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Campus Sud, Edifici C', C/Pasqual i Vila s/n, E-08028, Barcelona, Spain.

^c Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93040 Regensburg, Germany.

^d IQAC-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain.

batteries or accumulators) can be restored to their original charged status after discharge. The original charged condition is recovered through an electric current flowing in the direction opposite to the flow of current when the cell was discharged (Figure 1B).²⁰ Hall *et al.*²¹ reviewed the application of the most studied materials used for electrical energy storage through batteries and supercapacitors, all them related to synthetic polymers and ceramic compounds.

Inganäs and Admassie²² recently reported the need to implement renewable energy technologies, based on solar energy conversion and storage, using organic materials in countries with low human development index. More specifically, the own authors proposed novel supercapacitors and batteries for storing solar electricity to facilitate the development of regions near to the equator with rapid economic growth and large populations. They emphasized that these technologies would have an enormous impact on poverty eradication.

Storage of electrical energy in supercapacitors or in secondary batteries constructed using renewable materials is very attractive from an environmental point of view. Hence, replacement of organic solvents by water contained in gel-polymer electrolytes is highly desirable. In addition, this strategy results in a significant reduction of the device cost. Unfortunately, water-containing gel-polymer electrolytes, called hydrogel-polymer electrolytes, are limited by their operating potential-window, which is of only ~1.23 V. However, supramolecular biohydrogels are currently considered as an important part of the next-generation of materials to enter the era of supercapacitors and batteries.

These investigations provide indication of the current relevance of biohydrogels in the field of energy storage devices. Accordingly, this review is aimed to establish the state-of-the-art in such field, paying special attention to areas where further research is urgently necessary. Table 1 summarizes the main biopolymers reported in this review and the related reference.

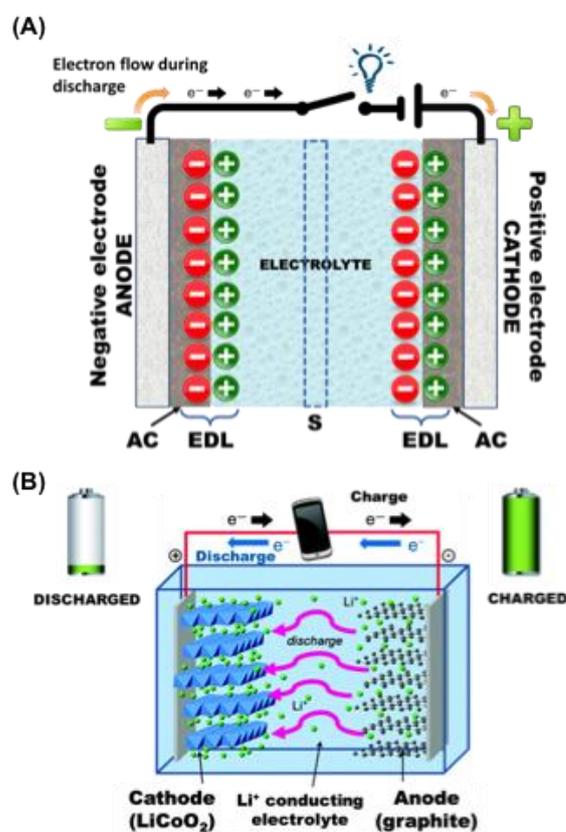
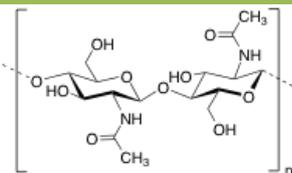
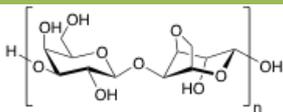
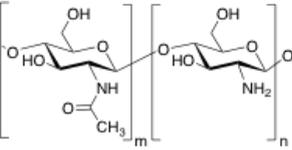
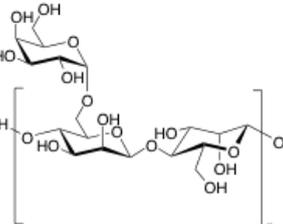
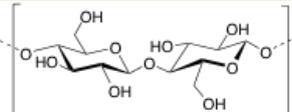
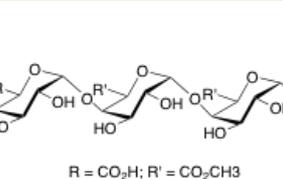
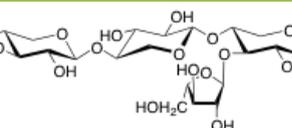
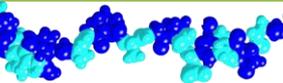
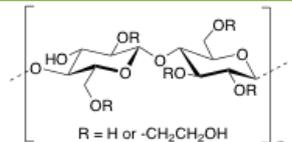
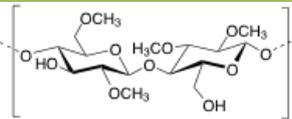
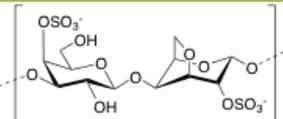
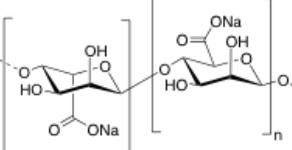
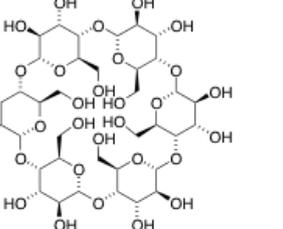


Figure 1. Schematic diagram of: (A) Charged electric double layer capacitor (AC: Activated carbon, EDL: Electrical Double Layer, S: Separator/porous membrane), and (B) example of the first-generation rechargeable lithium-ion cell. During charging, lithium ions flow to the negative electrode through the electrolyte and electrons flow from the external circuit. During discharge the directions are reversed. Adapted with permission from ref. 23. Copyright © 2014 Royal Chemical Society.

Table 1. Molecular structures of biopolymers used in the preparation of electrolytes and/or electrodes for electrical storage devices.

Biopolymer	Structure	Refs.	Biopolymer	Structure	Refs.
Chitin		25,27	Agarose		46
Chitosan		25,27, 28,30, 31,32	Guar gum		24
Cellulose		33	Pectin		48
Hemicellulose		36	Gelatin	 Mixture of peptides and proteins produced by partial hydrolysis of collagen	49,50
Hydroxyethyl-cellulose		37	DNA		51,52, 53
Methylcellulose		22	k-Carrageenan		58
Sodium alginate		45	alpha-Cyclodextrin		65

2. Polysaccharide-based hydrogels

Natural polysaccharides are being developed as alternatives to synthetic inorganic materials for electrochemical devices. Major attention has been recently paid to fabricate compact organic capacitors combining solid polymers with gel polymer electrolytes (GPE). For this purpose, hydroxylated, carboxylated, or sulphated-polysaccharides have been essentially used because of their high ionic conductivity and advantageous mechanical properties.²⁴

2.1. Chitin and chitosan

Among polysaccharides, the applicability of chitin and chitosan (CS), as biopolymers for conductive electrode and electrolyte has been explored. Chitin, which is the second most abundant biopolymer in the biosphere after cellulose²⁵ is a linear polysaccharide of α - or β -(1-4)-2-acetamido-2-deoxy-D-glucopyranose where the monomeric residue is *N*-acetylglucosamine.²⁶ It is found as structural material in, for example, fungal cell walls, insect and crustacean exoskeletons, mollusk radula, and cephalopod beaks.²⁷ Man-made chitin waste coming from seafood processing is used to produce commercially using processes involving harsh chemical treatment. Furthermore, biowaste from other sources, as for example those of mushroom, silk, and honey-harvesting industries, has been

recommended as a substitute for chitin obtaining. On the other hand, CS is derived from controlled chitin deacetylation. This material can be produced with a wide range of physical properties simply varying the chain length of the precursor material or the degree of chemical depolymerization and the extent of deacetylation. Both chitin and CS bear nitrogen- and oxygen-containing functional groups, that can be chemically modified, exhibit good biocompatibility and form uniform films and hydrogels. However, chitosan is by far the more widely used as biomaterial than chitin, including in hydrogel-based applications.²⁷⁻²⁹

CS has been used for the preparation of solid-state proton-conducting polymer batteries. However, due to its insolubility in water, CS is dissolved in acetic acid to provoke ionic conductivity. The transport of protons from acetic acid occurs through microvoids inside the biopolymers, which was probed through piezoelectric studies.³⁰ Different strategies have been explicitly developed for biopolymer processing and could be applied for the generation of chitin- or chitosan-based electrolytes or electrodes.²⁷ The scheme represented in Figure 2 depicts an example of such strategies.

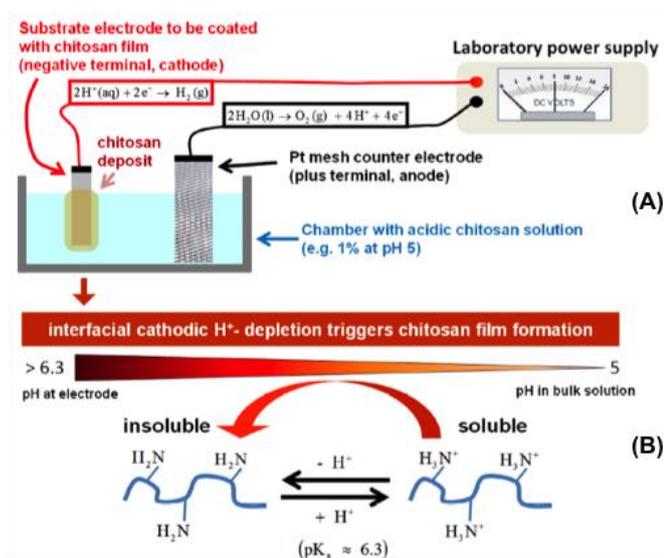


Figure 2. (A) Instrumental setup for electrodeposition of thin chitosan films on substrate electrodes, and (B) mechanism of chitosan precipitation onto cathode surfaces. Both illustrate easy methods for biopolymer electrodes obtaining. Adapted with permission from ref. 27. Copyright © 2013 American Chemical Society.

Among the pioneers in the preparation of either electrolytes or electrodes using biohydrogels for electrochemical energy-storage cells, Subramanian and co-workers³¹ deserve special mention. These researchers designed a solid-state electrical double layer capacitor combining a novel, cost-effective and eco-friendly electrode binder made of chitosan chemical hydrogel (CCH) and a separator consisting of ionically cross-linked chitosan hydrogel membrane electrolyte (ICSHME). The EDLC, which was prepared using 40% loading of CCH electrode binder and ICSHME with 1 M NaOH dopant, was assembled with black pearls carbon as electrode. The EDLC was cycled between constant current charging and constant current discharging until failure. Figure 3 reflects that such capacitor is stable during operation between 20 and 200

cycles. However, the capacity decreased with increasing number of cycles, even though it was not definitely exhausted until a large number of cycles (*i.e.* from 500 to 1400). This evidenced that the EDLC model works well but the charging/discharging stability needs improvement.

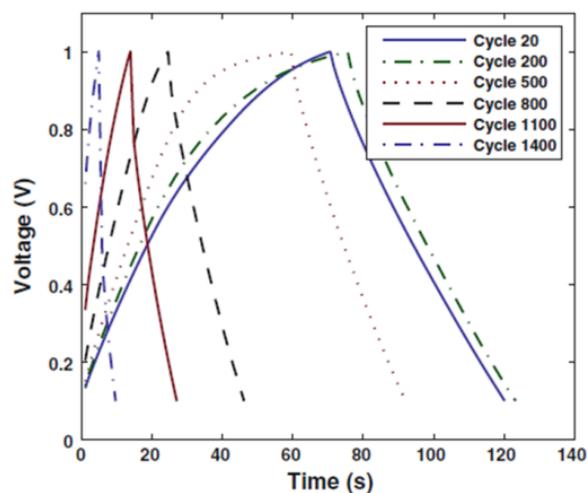


Figure 3. Charge/discharge plots for several cycling of the EDLC capacitor prepared as reported in ref. 31. Reprinted with permission from ref. 31. Copyright © 2012 Springer.

The same authors studied the design of polymer electrolyte membranes based on ionically cross-linked CS hydrogel prepared in reference³¹ to fabricate fuel cell. In this case, the CS was chemically doped by the addition of sulfate and hydrogen phosphate salts of sodium. The operating cell voltage decreased only 100mV, from about 0.8 to 0.7 V, during the 100 h period of continuous operation implying a good cell performance durability of the fuel cell.³² The application of chitosan to other energy storage devices needs to be explored.

2.2. Cellulose and derivatives

Cellulose is another powerful candidate for the design of new electrolytes for electronic devices. This is the most abundant biopolymer in nature. Cellulose was discovered in 1838 by the French chemist Anselme Payen, who isolated this biopolymer from plants determining its chemical formula. Cellulose is a good candidate for electrode and electrolyte preparation since it strongly binds organic and inorganic materials, such as conducting polymers (CPs),³³ graphene oxide (GO)³⁴ and carbon nanotubes (CNTs).³³

Development of environmentally friendly methods for “green” cellulose extraction and approaches for suitable cellulose dissolution are requirements to be consistent for the green use of this biopolymer. Within this context, several researchers have used ionic liquids, such as 1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride, to dissolve cellulose. Other interesting approach is the microwave heating, which significantly accelerates the cellulose dissolution process and allows the separation of cellulose from other lignocellulosic materials, like lignin and hemicellulose. Main green approaches were early reviewed by Zhu *et al.*³⁵

In addition, several cellulose derivatives, such as hemicellulose and hydroxyethylcellulose (HEC), have been also explored in the field of capacitors. Hemicellulose consists of a branched polymer bearing 500-3000 sugar units per polymer chain, whereas cellulose is unbranched and involves 7000-15000 glucose units per polymer chain. Recently, electrically conductive hemicellulose hydrogels (ECHHs) have been prepared by a one-pot reaction between biocompatible *O*-acetyl-galactoglucomannan and aniline pentamer, using epichlorohydrin as crosslinking agent. This simple and green

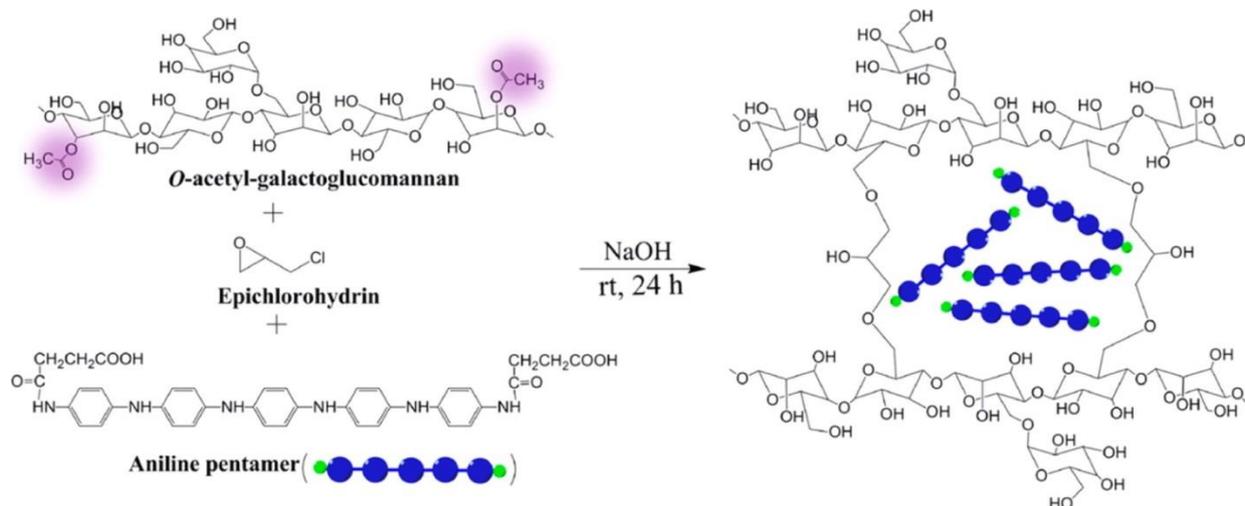


Figure 4. Schematic synthesis of ECHHs using epichlorohydrin as a cross-linker in basic media. Reprinted with permission from ref. 36. Copyright © 2014 American Chemical Society.

Rosi *et al.*³⁷ combined hydrogel-polymer electrolytes based on polyvinyl alcohol (PVA) with HEC for the preparation of capacitors. HEC products are water-soluble polymers with particular abilities. They are thick, retain water, form films, exhibit pseudoplastic solution behavior and tolerate salts. The content of HEC in the hydrogel polymer electrolyte used for the preparation hydrogels was 1, 2.5, and 5 wt.%. The highest capacitance (160 F g^{-1}) was obtained using the hydrogel with 1 wt.% of HEC and corresponded to the electrolyte with the lowest ohmic resistance, which was attributed to the rapid ionic transport offered by the O-H groups throughout the chain of HEC in the electrolyte. However, the specific capacitance decreased with increasing concentration of HEC. This behavior was related to the reduction of free-volume in the hydrogel-polymer electrolyte with 2.5 and 5 wt.% of HEC. Those observations were in accordance with the results of Sampath *et al.*,³⁸ who used PVA-based membranes doped with HClO_4 as electrolytes for electrochemical capacitor. It should be noted that the specific capacitance reported by Rosi *et al.*³⁷ was similar to that obtained with synthetic organic gels (about $150\text{-}250 \text{ F g}^{-1}$), even though such values are not yet competitive with those described for metal oxides (about $700\text{-}1500 \text{ F g}^{-1}$).^{17,39}

On the other hand, bacterial cellulose (BC) is an interesting eco-friendly biomaterial produced by various microorganisms (*e.g.* *Acetobacter xylinum*, *Pseudomonas*, *Rhizobium* and *E. coli*) that can be produced at industrial scale via the microbial fermentation process.^{40,41} BC is made of ultrafine nanofibers, with a diameter of less than 100 nm, arranged forming an ultrafine network that confers unique properties (*e.g.* as porosity and high

approach, which occurs in water and at ambient temperature, is illustrated in Figure 4.³⁶

Albertsson and co-workers³⁶ found that the presence of aniline pentamer (AP) inside the biohydrogel allow the preparation of a *p*-type semiconductor. The presence of holes and its concentration was found to increase with the AP, leading to improve the conductivity. Those results represented an important achievement for the development of new biohydrogel electrolytes from hemicellulose materials.

biodegradability, tensile strength and water retention capability). Renewable, biodegradable and electro-conducting composites have been obtained by combining BC with CPs (*e.g.* polyaniline, polypyrrole). The mass specific capacitance of these materials, which were obtained by in situ polymerization of the corresponding monomers at 0.2 A g^{-1} , ranges from 273 F g^{-1} to 316 F g^{-1} .^{42,43} These interesting results obtained with BC will be addressed in detail in the section 4.

The research developed up to now demonstrate that natural cellulose and its derivatives can be employed to avoid the presence of toxic and volatile organic solvents in the battery electrode fabrication process, while being compatible with the aqueous processing of hydrogel electrodes.

2.3. Alginate

Alginates are a family of water-soluble polysaccharides (carbohydrate polymers), extracted from brown seaweed. These materials were commercialized over 50 years after they were first investigated in the late 19th century by the British chemist E.C. Stanford. Alginates have been mainly used by the pharmaceutical industry for specific gelling, thickening, and stabilizing applications.

Alginates are heteropolysaccharides with a block-copolymer structure that involve building blocks made of mannuronic acid (M) and guluronic acid (G) monomers. Thus, the block-copolymer is composed of longer homopolymeric blocks of M and G alternated with shorter blocks with a sequential M-G distribution. The proportion, distribution and length of such blocks are crucial

because of their implications in the properties of the material. While G-blocks are responsible of the gel-forming capacity, MM and MG units provide flexibility to the polymer chains. Composition of the blocks depends on the species used for extraction and the part of the thallus from which extraction is made. The acid, which is extracted from seaweed, is converted into the sodium salt that, then, is extracted from the thick slurry, heavily diluted, and filtered to remove the unwanted inorganic residues. Sodium alginate (SA) obtained using this procedure can then be used to produce other useful salts, as for example potassium and calcium alginates. Nowadays, the main alginate producers are Scotland, Norway, China and the USA, followed by Japan, Chile, and France.

The number of studies related with the application of alginate hydrogels for energy-storage devices is very scarce. These studies are mainly devoted to the development of new electrodes and the improvement of the capacity cycle-life in Li-ion batteries. Taking into account the electrode materials used for the fabrication of lithium-ion batteries, there is an enormous interest in solve failure mechanisms, such as electrode pulverization and cracking, associated to charge/discharge cycles. Although the specific capacity of silicon is ten times higher than that of graphite, anodes made of the former material undergo fast capacity decay and short cycle-life. This has been attributed to the volumetric expansion

experienced by silicon upon full lithium insertion (lithiation) and the significant contraction on lithium extraction (delithiation). These drastic volumetric variations can provoke cracking and pulverization in the electrode, leading to both loss of electrical contact and excessive solid–electrolyte interphase growth.⁴⁴ Accordingly, development of more resistant electrode materials has become necessary. Different materials have been proposed as polymeric binders for Si-based anodes: poly(divinylidene fluoride) (PVDF), carboxymethyl cellulose (CMC), poly(acrylic acid) (PAA), polyamide imide, polyamide amine,⁴⁴ SA, etc. Kovalenko *et al.*⁴⁵ evidenced that Si nanoparticles coated with SA binder result in a stable silicon electrode with volumetric capacity ($\sim 1520 \text{ mA h cm}^{-3}$) higher than that obtained using other binders, such as PVDF, PAA, and CMC.

Thus, SA had a positive impact on the cycle performance of the Li-ion battery. Figure 5 compares the electrochemical behavior of SA with that of the electrode without binder as well as with those obtained using other polymeric binders. As it can be seen, the electrochemical stability of silicon nanoparticles coated with SA does not decrease after the first cycle, behaving so electroactive as the electrode without binder (Figure 5d).

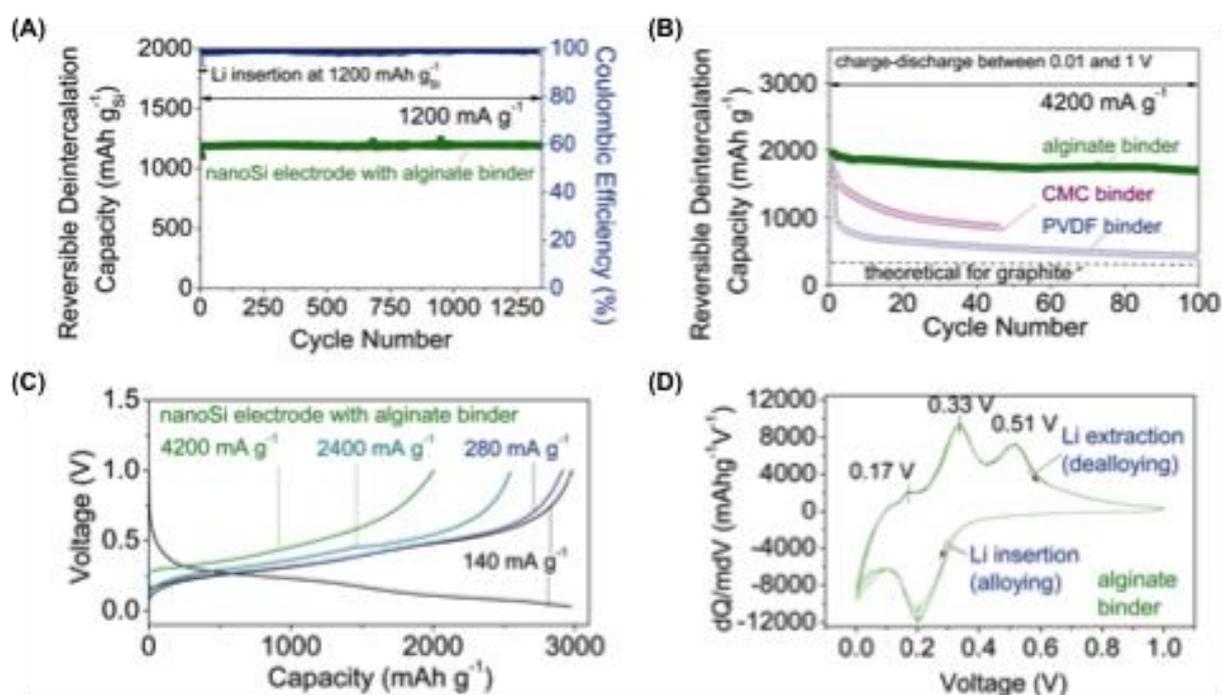


Figure 5. Electrochemical performance of alginate-based nano-Si electrodes (electrode density = 0.50 g cm^{-3} , weight ratio of Si:C = 3:1). (A) Reversible Li-extraction capacity and CE of the nano-Si electrodes *versus* cycle number for Li insertion level fixed to 1200 mA h g^{-1} Si. (B) Reversible Li-extraction capacity of nano-Si electrodes with alginate, CMC, and PVDF binders *versus* cycle number collected for the current density of 4200 mA g^{-1} for cells cycled in the potential window of 0.01 to 1 V *versus* Li/Li⁺. (C) Galvanostatic discharge profiles of the nano-Si electrode at different current densities between 0 and 1 V. (D) Differential capacity curves of the nano-Si electrode in the potential window of 0 to 1 V *versus* Li/Li⁺ collected at the rate of 0.025 mV s^{-1} after the first galvanostatic charge-discharge cycle. All electrochemical measurements were performed at room temperature in two-electrode coin-type half-cells. In (A), the capacity is reported for the Si contribution only. In (B) to (D), the capacity is normalized by the total weight of Si and C additives. Adapted with permission from ref. 45. Copyright © 2011 American Association for the Advancement of Science.

In general, conventional hydrogels cannot be used as electrode materials because of their inherent poor mechanical integrity.

However, the chemical structure of SA, which contains a large number of hydroxyl groups, facilitates its application not only as

polyelectrolyte but also as electrode material in presence of other conductive particles (*e.g.* CPs, carbon black and metal particles). Thus, the favorable mechanical strength has been attributed to inter- and intramolecular hydrogen bonding interactions between SA chains and to the attractive electrostatic interaction inside the entanglement among SA chains and conductive particles, the latter being also responsible for the conductive properties. The fabrication of CP-SA hydrogel electrodes for supercapacitors and the synergistic interaction between SA and CP will be discussed in section 4.

2.4. Other polysaccharides

Considering the limited mechanical properties of common hydrogels, discussed before, biobased gels represent an alternative for the fabrication of stable electrolyte and electrode systems for use in supercapacitors and secondary batteries devices. Moon *et al.*⁴⁶ recently reported a simple procedure to prepare NaCl-agarose-gel (AGAR)-mediated MnO₂ hybrid electrolyte with high potential for large scale fabrication (scale-up), cost-effectiveness, safe, nontoxic and flexible supercapacitors (Figure 6). An agarose-based hydrogel is a gelling constituent of agar with an agarobiose monomeric unit,⁴⁷ which features submicrometer pores (*i.e.* sizes of 400–500 nm), high elasticity (*i.e.* elastic modulus of 116 kPa), low in cost, and is environmentally benign.

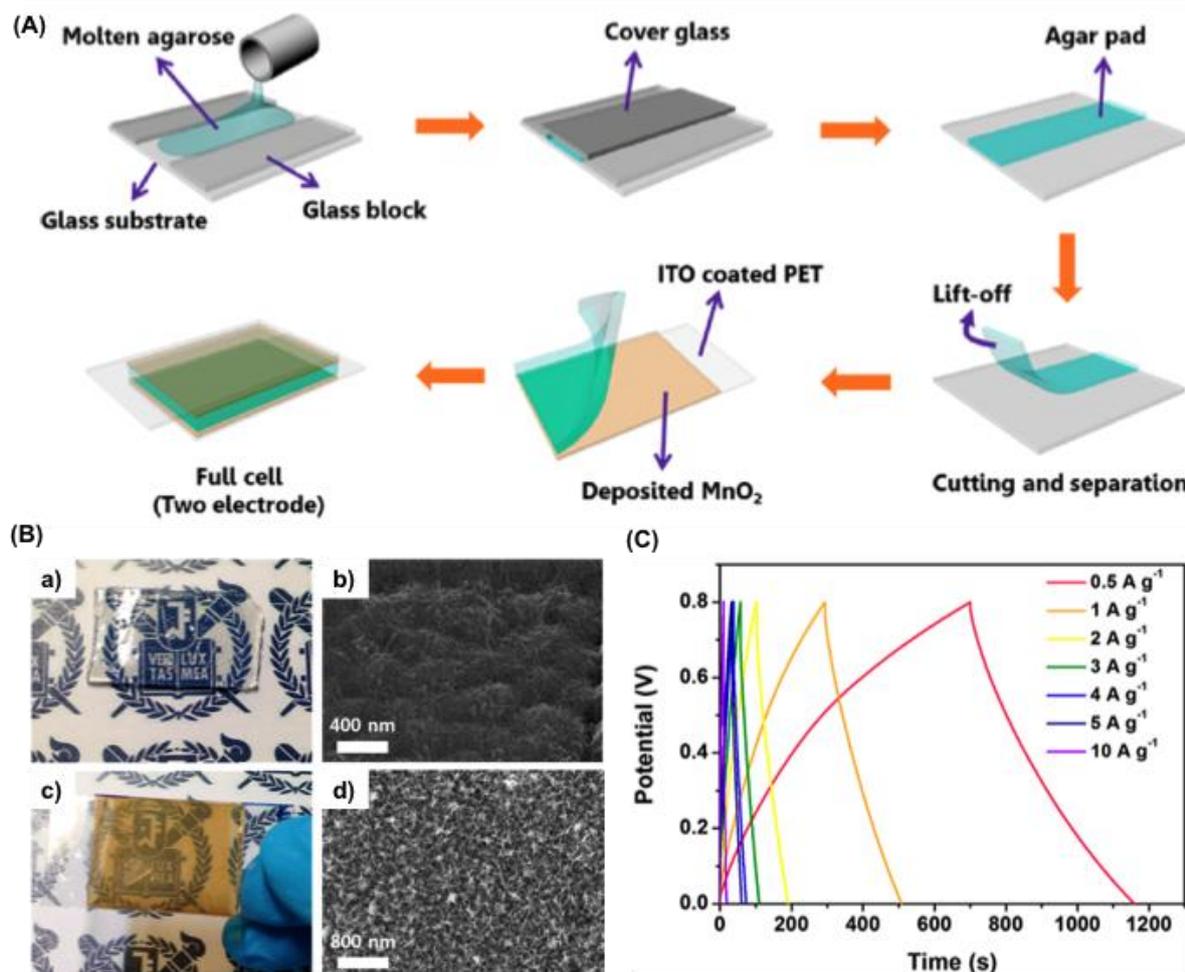


Figure 6. (A) Schematic illustration showing the fabrication of an agarose-gel-mediated MnO₂ symmetric cell assembly. (B): a) Optical image and b) SEM surface image of agarose gel; c) optical image and d) SEM surface image of MnO₂ thin film deposited onto ITO-PET substrate. (C) Charge/discharge profile of NaCl-AGAR supercapacitor assembled between two electrodeposited MnO₂ electrodes. Adapted with permission from ref. 46. Copyright © 2015 American Chemical Society.

Among the advantages of NaCl-AGAR, its transparency deserves special mention. In order to characterize the implications of its flexibility, a one-planar interdigitated prototype of supercapacitor was designed to check the electrochemical response upon compressive bending and tensile bending.⁴⁶ Analyses, which were performed combining cyclic voltammetry and electrochemical impedance measurements, did not show significant deviations in the electrochemical behavior. The excellent supercapacitive behavior of the flexible NaCl-AGAR-based supercapacitor as full cell

was attributed to the porous structure of that material, which provided several advantages for ion transport (Figure 6b). Charge and discharge galvanostatic curves displayed symmetric triangular forms with a small internal resistance drop in a broad range of current densities, demonstrating excellent rate capability (Figure 6c).⁴⁶ Additionally, authors fabricated NaCl-AGAR supercapacitors enveloped with poly(ethylene terephthalate) (PET) sealant tape and sticky polypropylene tape. These devices revealed enhanced ability to maintain normalized capacitances, as revealed by the very slight reduction observed after 600 cycles as well as the fact maintained

80% of the maximum capacity after 1200 cycles. In contrast to the high stability of enveloped supercapacitors, open systems presented a continuous decay after only 400 cycles (Figure 7). Accordingly, Moon *et al.*⁴⁶ proved that the fabrication of almost 100% biohydrogel supercapacitors is feasible and needs further studies.

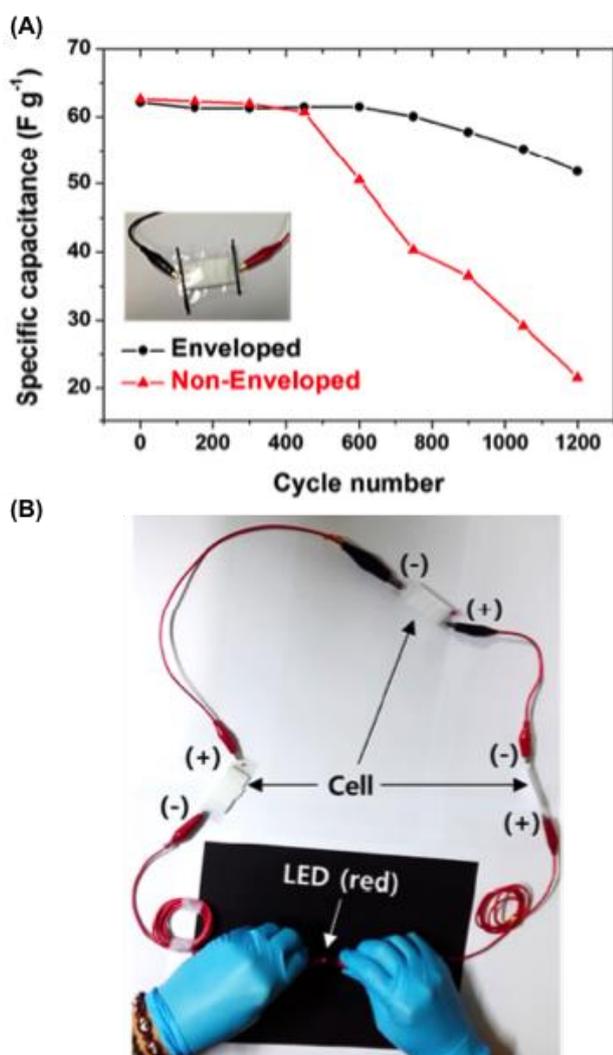


Figure 7. (A) Long cycle-term stability test profile of enveloped and non-enveloped NaCl-AGAR supercapacitors, performed at a scan rate of 100 mV sec^{-1} and (B) digital photo of an LED activated by the NaCl-AGAR supercapacitor. Reprinted with permission from ref. 46. Copyright © 2015 American Chemical Society.

Sudhakar *et al.*²⁴ employed guar gum (GG) as GPE for the fabrication of supercapacitors. GG is a non-ionic, hydrophilic, galactose- and mannose containing polysaccharide (*i.e.* it belongs to the galactomannans family). The linear backbone involves β 1,4-linked mannose residues, galactose residues forming short side-branches through 1,6-links to every second mannose. GG forms highly viscous solutions when hydrates in cold water. This unique property is crucial for the employment of GG as GPE in supercapacitors cells.

For the construction of the supercapacitor cell Sudhakar *et al.*²⁴ used GG as gel and binder, glycerol as plasticizer, lithium

perchlorate (LiClO_4) as dopant salt and activated carbon (AC) derived from areca fibres, an abundantly available fibre extracted from *Palmecea* plants, as electrode material. The GPE was sandwiched between two prepared AC coated electrodes. The unit cell was sealed in a plastic coated aluminium pouch keeping the two wires outside. Amazingly the GG gel exhibited an unusual tubular array like morphology without crystalline and/or phase separation, and showed a great stability in aqueous medium. Unfortunately, the capacitor charge-discharge profile, as measured by galvanostatic method, evidenced that the energy density and power density were not remarkable in comparison to other biohydrogels.

Channel type mesoporous architecture represents an adequate morphology for high power supercapacitor electrode applications, which has promoted the exploration of sophisticated materials, especially hybrid organic-inorganic compounds. Wahid *et al.*⁴⁸ reported the template based synthesis of supercapacitive carbon by infiltrating a natural hydrogel, pectin, in mesoporous silica template and, subsequently, applying pyrolysis in inert atmosphere (SBA-15). Pectin is an indigestible soluble fibre that combined with water forms colloidal systems and gels, which are frequently used as ingredients in food technology (*e.g.* it provides smooth and sticky texture to jellies and jams). From a chemical point of view, pectin is a biopolymer rich in 1,4-linked α -glucuronic acid units, having its carboxylic group esterified. This biomaterial exhibits higher performance than other gels (*e.g.* resorcinol, PVA, polyvinylpyrrolidone, agarose or alginate) as a precursor for the carbon synthesis because the concentration of hydroxyl groups is adequate to interact with water and with the template walls via hydrogen bonds. Indeed, pectin hydrogel gives places to unbreakable columns inside silica channels with less sideways diffusion, fulfilling all the necessary requirements for the transformation into one dimensional carbon threads. Wahid *et al.*⁴⁸ doped the carbon-pectin activated electrodes with urea molecules, which also increased the viscosity due to the formation urea-pectin chains interactions. Indeed, the compactness of the electrode increased with the viscosity since the sideways flow decreased, even at higher temperatures. This study clearly probed that the electrode morphology, with nanometric mesoporous channels, exerts a crucial role in the performance of the capacitor (Figure 8). On the other hand, Wahid *et al.*⁴⁸ also compared the stability of pectin-containing electrodes in terms of capacitance by applying 2000 consecutive charge-discharge cycles. Si-carbon-pectin electrodes (PU-SBA11) retained 96% of their capacitance at a current density of 10 A g^{-1} (Figure 9). This cycling stability was higher than that observed for other activated carbon electrodes prepared from agarose and alginate gels (AgU-SBA11 and AlU-SBA11, respectively). Similarly, electrodes prepared using pectin gels had better electrochemical behavior than those derived from other gels. This superiority was attributed to the particular chemical structure of pectin, which presents additional hydrogen bonding centres in comparison with agarose and alginate.

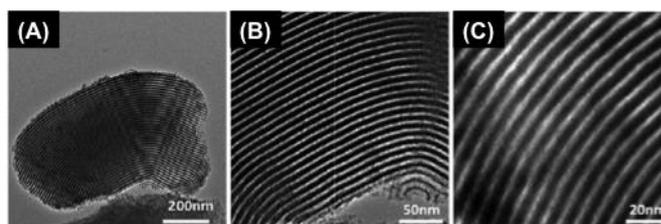


Figure 8. TEM micrographs, with increasing magnification from (A) to (C), of pure SBA-15 template prepared with pectin-urea. Adapted with permission from ref. 48. Copyright © 2015 Royal Chemical Society.

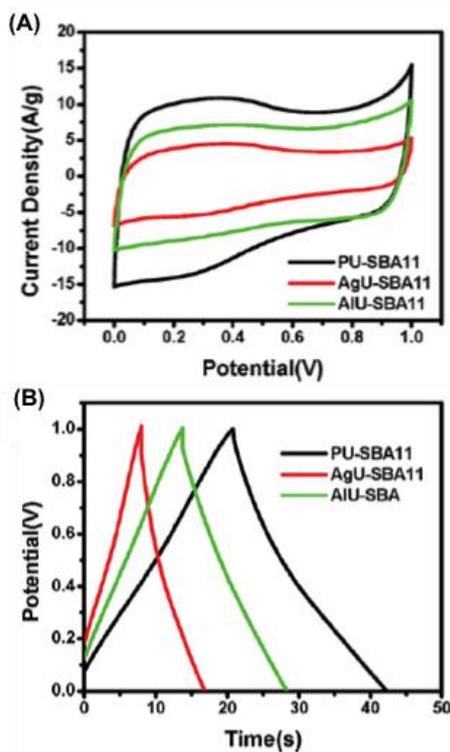


Figure 9. Electrochemical performance comparison of three natural gels, namely agarose, alginate and pectin, on a three assembly in 1 M H₂SO₄ with calomel as reference electrode: (a) compares the CV behavior at scan rate of 50 mV s⁻¹, showing high electrochemical stability for pectin-based electrode; and (b) compares charge-discharge characteristics at 10 A g⁻¹ for the three biohydrogel systems studied in this work. Adapted with permission from ref. 48. Copyright © 2015 Royal Chemical Society.

Overall, results recently reported in the literature suggest that in general polysaccharides represent a versatile alternative to conventional metal-oxides materials currently employed to fabricate energy-storage devices.

3. Lignin and quinone

Lignin is the major byproduct of paper and pulp industry because it is present in the cell walls of woody plant matter.

4. Protein-based hydrogels

Gelatin is a combination of random coiled peptides and proteins that result from the hydrolysis of collagen triple helix. Consequently, the chemical structure of gelatin resembles that of collagen, presenting a high amount of glycine, proline and hydroxyproline residues. Gelatin dissolves in hot water, forming a pale yellow, semi-transparent and viscous solution, while a hydrogel is obtained by cooling down below 308 K. This biopolymer exhibits

high stability against electrolytes, effective adhesion and ease dispersion of positive electrode materials. In spite of such advantageous characteristics, gelatin is frequently limited by its intrinsically poor mechanical strength, improvement being required, for example through chemical cross-linking.

Gelatin has been recently developed as a binder for graphite electrodes in Li-ion batteries.⁴⁹ Cathodes using gelatin present better capacity and cyclability than those obtained using synthetic polymeric binders. On the other hand, Choudhury *et al.*⁵⁰ developed gelatin hydrogel electrolytes (GHEs) by cross-linking an aqueous solution of gelatin with aqueous glutaraldehyde for application as electrolyte in supercapacitor cells. These authors obtained light brown, semi-transparent, and mechanically strong freestanding films with a large volume of water absorbed in the polymer hydrogel matrix. The morphology of GHE films was found to change when current was applied, their charge-discharge capacity improving upon the addition of NaCl as dopant. The ionic conductivity of pristine GHE was explained by considering that protons associated to amino, hydroxyl and thiol groups, as well as readily removable small chain fragments, migrate through the hydrogel under the influence of a small electric field. On the other hand, the ionic conductivity in NaCl-doped GHEs is predominantly due to the free diffusion of hydrated Na⁺ and Cl⁻ ions inside the biopolymer matrix. This effect is illustrated through the variation of the specific capacitance, which increased from 37.6 to 81.2 F g⁻¹ when the concentration of NaCl in the GHEs was modified from 0 to 3 N.⁵⁰ A comprehensive review of hydrogel-polymer electrolytes for electrochemical capacitors was reported by the same authors.¹⁷

Despite the tremendous improvements in the development of batteries and supercapacitors, materials of different chemical nature are still necessary to assemble an electronic device for energy storage. Within this context, researchers have used both hard materials, such as metals, and very soft materials, such as hydrogels. However, the use of the most important biological molecule in life, DNA, exceeds science fiction.

Luo and co-workers,⁵¹ from Cornell University, were pioneers in the preparation of mechanically stable DNA-hydrogels. This was achieved by modifying the biomolecule with a polymerase enzyme that provoked the elongation of DNA chains, weaving them non-covalently into the hydrogel. The new hydrogel, which was termed meta-hydrogel (recalling the concept of metamaterials), exhibited liquid-like properties when it was taken out of water and solid-like properties, when it was in water. DNA-based meta-hydrogels presented a hierarchical internal structure that was useful for different potential applications. Among them, authors explored the behavior of the biohydrogel doped with gold nanoparticles in an electrical circuit, employing water as switch (Figure 10).

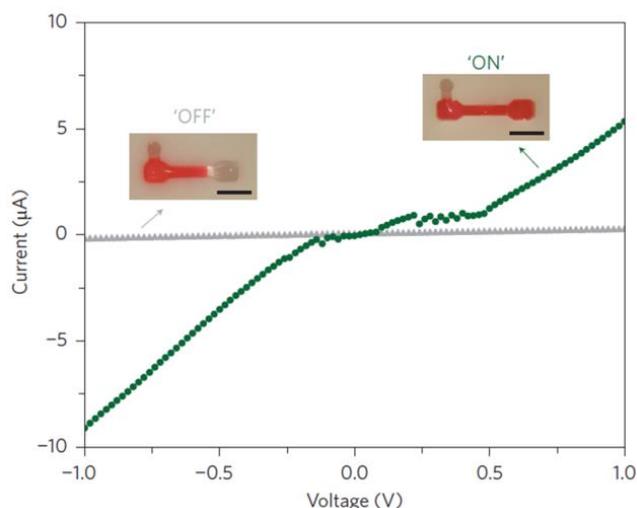


Figure 10. Electric circuit switch formed using the liquid- and solid-like properties of DNA meta-hydrogel. When the DNA meta-hydrogel (containing 10 nm gold nanoparticles) has liquid-like properties, the circuit can be covered by the gel (green circles, 'ON'). By simply adding water, the gel metamorphoses to its original shape, which is shorter, resulting in the gel rapidly moving away (within seconds) from the electrode and completely shutting off the current (grey triangles, 'OFF'). Scale bars (insets), 5 mm. Reprinted with permission from ref. 51. Copyright © 2012 Macmillan Publishers Limited.

Regarding with the innovative research developed by Luo and co-workers,⁵¹ Hur *et al.*^{52,53} used the same concept to create supercapacitors with layer-by-layer (LBL)-deposited polyelectrolyte multilayers (PEMs). These were prepared combining DNA hydrogel (Dgel) with either poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) or polyaniline (PANI) (Figures 11 and 12). These capacitors could be directly dipped in physiological fluids in a very small package form and be operated with a great performance, which represent important advantages. Furthermore, these devices showed very stable galvanostatic charge-discharge cycling response in artificial urine and PBS solutions. When the number of cycles reached 1000, the initial capacitance of PEM_{1,0}, PEM_{3,0}, and PEM_{5,0}-DNA hydrogel, respectively (subscript numbers represent the repeated LBL PEM depositions) decreased by only 71, 84, and 89%, respectively. It should be remarked that, although studies in this field are still at the initial stages, one can anticipate that successful applications in living organisms will be achieved in a close future. Although these studies are still in their beginning one can anticipate that a real application in living organisms would not be far from being achieved.

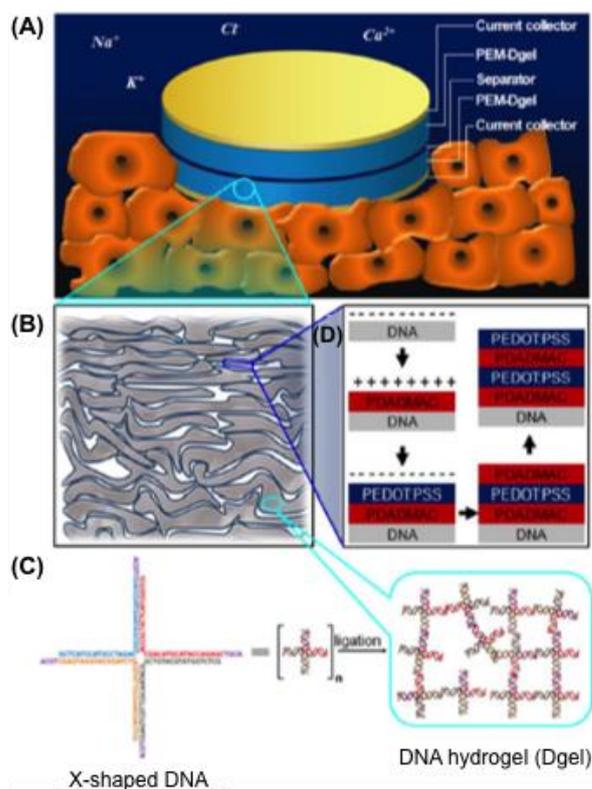


Figure 11. Schematic representation of, (A) PEM-Dgel supercapacitor operation in physiological environment (stacked features underneath the device display the cells). (B) Enlarged detailed structure of PEM-Dgel where porous layered Dgel (grey) is covered by conductive PEM (indigo), (C) Magnified view of Dgel where X-shaped double stranded DNAs are crosslinked by enzymatic reaction, (D) Construction of PEM-Dgel electrodes by coating the Dgel with the polyelectrolyte pair polydiallyldimethylammonium chloride and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PDADMAC/PEDOT:PSS) using LBL deposition. Reprinted with permission from ref. 52. Copyright © 2015 Nature Publishing Group.

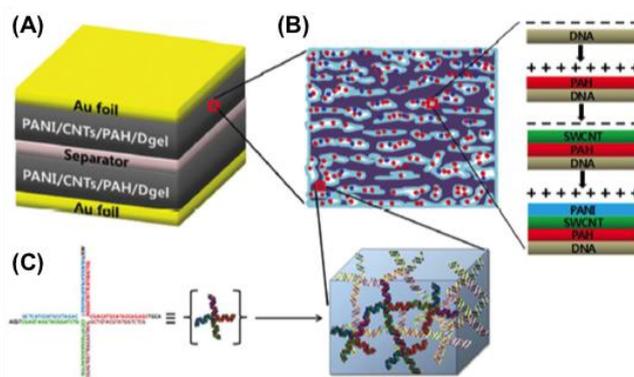


Figure 12. Schematic illustration of the sophisticated DNA gel-based supercapacitor developed by Hur and co-workers. (A) Capacitor assemble was done by immersing the dried Dgel into the positively charged PAH solution. Negatively charged CNTs and positively charged PANI were electrostatically assembled to form a porous conductive and pseudocapacitance layer, respectively. Each film

was performed by the conventional layer-by-layer (LBL) deposition process on top of Au foils. (B) Detail of the conversion of insulating Dgel into a conductive Dgel by electrostatic deposition of poly(allylamine hydrochloride) (PAH), carbon nanotubes (CNT), and PANI explained in (A). (C) Representation of the DNA building block (X-shaped DNA) consisting of Dgel phase. Adapted with permission from ref. 53. Copyright © 2013 Royal Chemical Society.

5. Hydrogels made from biopolymers and electroactive conducting polymers

The main advantages associated to the incorporation of CPs into non-conducting hydrogels matrices are the achievement of large conducting surface areas and fast electron-ion transfers. Further, CP-based biohydrogels fulfill the requirements of 3D-self-supported structures for anode and cathode manufacturing (*i.e.* they eliminate the need of binders or conducting fillers discussed in previous sections).

As it has been reported, PANi, polypyrrole (PPy) and PEDOT improve the power density of supercapacitors. Accordingly, a large number of works available in the literature describes the combination of CP with isolating synthetic polymers.⁵⁴⁻⁵⁷ Nevertheless, studies related with the synergistic relationship between biopolymers and CPs are very scarce.

In a recent work, we have reported a comprehensive study of the use of κ -carrageenan (κ C), sodium alginate, chitosan and gelatin hydrogels as electrolytic media, PANi nanofibers (PANi-nfs) acting as redox additive into the biohydrogel, and PEDOT-supported stainless steel as active electrodes.⁵⁸ Among these green electrolytes, κ -carrageenan was the biohydrogel with the best electrochemical behavior, with good specific capacitance, small leakage current and high cycling stability. The maximum energy density, which is the amount of energy stored per unit of mass, and the power density, which represents the speed at which the energy stored can be delivered; were 6.1 W h kg^{-1} and 1700 W kg^{-1} for κ C-PEDOT system, respectively. Figure 13 shows the schematic representation of the complete supercapacitor system (A), as well as the building of four assembled organic electronic supercapacitor OESC- κ C device connected in series to power a light emitting diode (LED) (B).

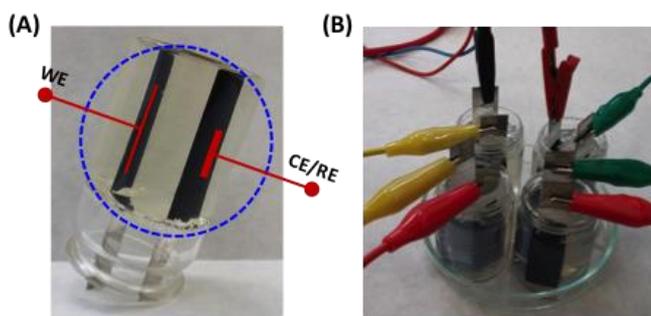


Figure 13. (A) One electrochemical cell fabricated with κ -carrageenan as electrolyte and both counter-electrode (CE) and work-electrode (WE) made of PEDOT conducting polymer. The reference electrode (RE) was directly contacted with the WE in the charge-discharge experiment. (B) Four-assembled electrochemical

cells, similar to that shown in (A), connected in series with electrical cables.⁵⁸

As mentioned in section 2.2, bacterial cellulose (BC) is one of the promising polysaccharides to be used in energy storage devices. Within this context, highly conductive BC composites were prepared with PPy⁴³ and PANi^{42,59} for supercapacitor applications. For this purpose, a simple procedure based on the *in situ* synthesis of the conductive electrodes by oxidative polymerization using BC as a template was employed. The resulting CP-coated BC nanofibrils formed uniform and flexible membranes due to the structure of BC, which consists on ribbon-shaped ultrafine nanofiber networks (Figure 14). These studies provide a straightforward method to prepare conducting thin films with good mechanical properties, which could be successfully used for the fabrication of flexible electrodes.

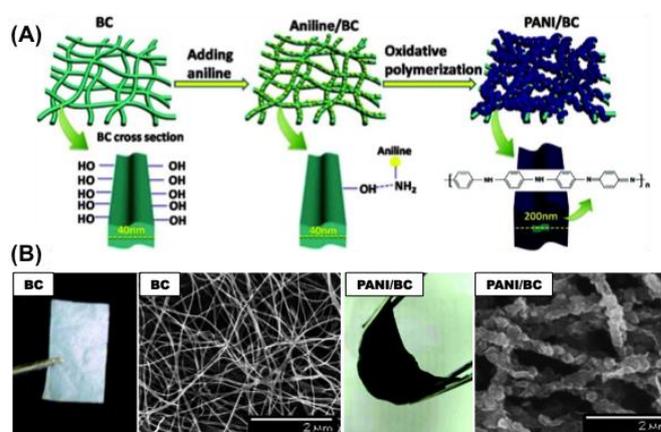


Figure 14. (a) Schematic illustration showing the fabrication of a flexible BC/PANI nanocomposite membrane. (b) Optical images and SEM images of pure BC and the BC/PANI composites after 90 min of oxidative polymerization reaction. Reprinted with permission from ref. 59. Copyright © 2011 American Chemical Society.

Flexible films prepared with BC/PPy showed higher conductivity than BC/PANI (77 and 5.1 S cm^{-1} for the former and the latter, respectively).^{42,43} However, both BC/PPy and BC/PANI hybrid electrodes were found to exhibit very high stabilities, retaining about 88.2% (278.7 F g^{-1}) and 94.3% (234.7 F g^{-1}) of the initial capacitance after 1000 cycles, respectively. This behavior was attributed to both the ordered structure of the composites and the strong interactions between the BC core and CP shell. The high electrochemical stability of BC/PANI and BC/PPy nanocomposites is illustrated in Figure 14 by means of galvanostatic charge/discharge curves. As it can be seen, the profiles registered during the charge and discharge processes are almost symmetric, indicating good pseudocapacitance behavior for the two BC/CP electrodes.

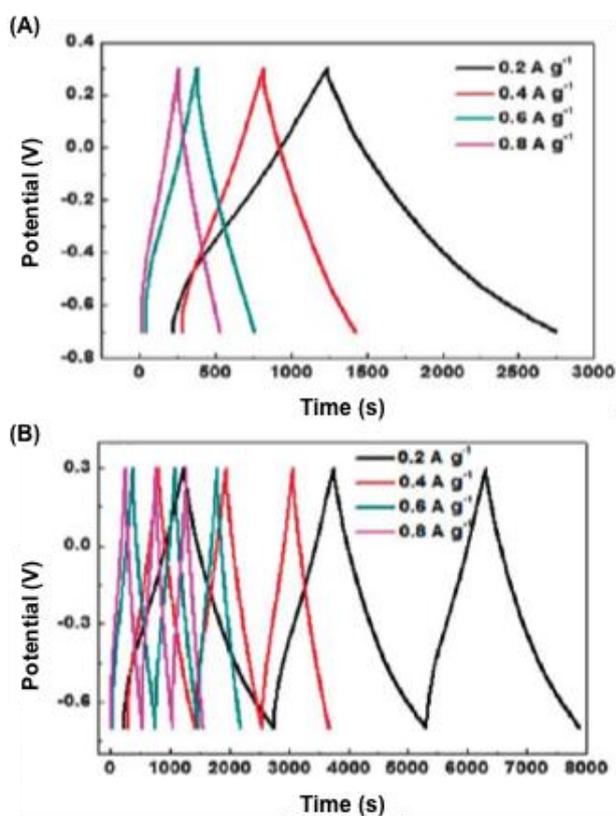


Figure 15. Cycle life of BC/CP composites at varied current density: (a) BC/PAni in 1 M H₂SO₄ solution; and (b) BC/PPy in 0.5 M KCl solution. Reprinted with permission from ref. 42 and 43. Copyrights

© 2012 American Chemical Society and 2013 Royal Chemical Society, respectively.

Supercapacitors based on freestanding and flexible electrodes derived from BC and PAni and activated with multiwalled carbon nanotubes (MWCNTs) have also been prepared using an easy and scalable synthetic method.³³ In this case PAni deposition was performed by anodic polymerization.³³ On the other hand, growth of PPy in cellulose paper by chemical polymerization was also proved to produce conducting materials. Such materials were successfully used to build supercapacitors and batteries.²⁰ Unfortunately, research using other CPs is much less explored.

Among polysaccharides, alginate has been recently investigated with conjugated polymers, specifically SA. Li *et al.*⁶⁰ described the electrochemical properties of PAni-SA nanofibers, which were prepared by oxidative polymerization of aniline and ammonium persulfate previously introduced into a dilute solution of SA (0.025–0.2 wt%). The new conducting biohydrogel was used as electrode material for supercapacitors assemblies. These PAni/SA electrodes exhibited an excellent specific capacitance (as high as 2093 F g⁻¹), long cycle life, and fast reversible oxidation/reduction on high current charges. Such remarkable electrochemical characteristic should be attributed to the nanostructure of the electrodes, which presented high electrode/electrolyte contact areas and short path lengths for electronic transport and electrolyte ion. Figure 15 displays the electrochemical response of the PAni/SA biohydrogels. This simple approach could be easily extended to fabricate nanostructured composites for supercapacitor electrodes or electrolyte materials.

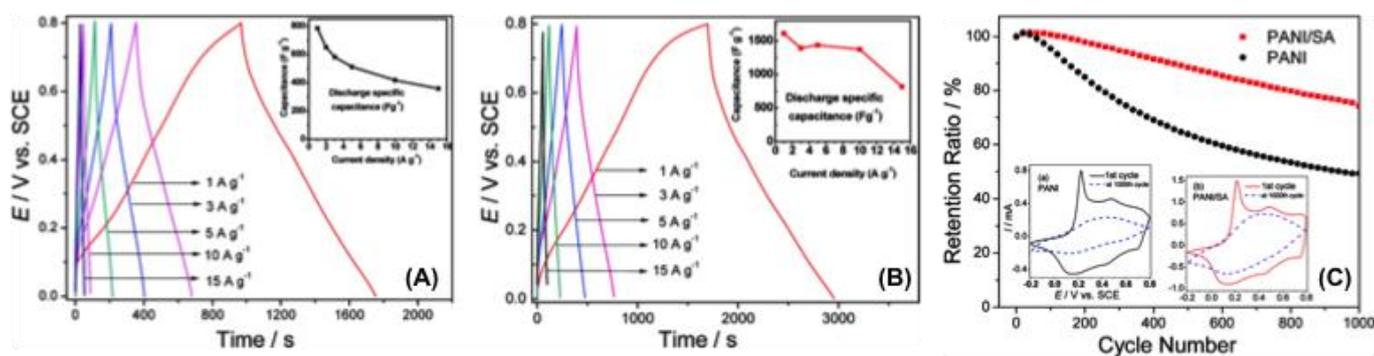


Figure 16. Galvanostatic charge/discharge curves of the (a) pure PAni electrode, (b) PAni/SA electrode at various current densities in 1M H₂SO₄; and (c) Cycling stability of PAni and PAni/SA electrodes at 100 mV s⁻¹ and insets are CV curves of PAni (left) and PAni/SA (right) after the first charge/discharge test and at 1000 cycles. Reprinted with permission from ref. 60. Copyright © 2011 American Chemical Society.

Yang and co-workers⁶¹ used the same procedure, the *in situ* polymerization of aniline in an aqueous solution of SA, to prepare reinforced PAni/SA conducting hydrogels. The main advantage of their system, which was based on the use of highly concentrated solutions of SA and aniline (2 wt%) in comparison to the dilute solution employed by Li *et al.*,⁶⁰ was the achievement of mechanically stable gels (Figure 17). After 1000 consecutive charge-discharge cycles, the retained specific capacitances and the

compressive tablets of PAni/SA hydrogels with high content of SA were found to be 71% and 76%, respectively. The good cycling stability of PAni/SA hydrogels was due to their substantial mechanical strength. As discussed above, both the interactions between the components of the system and the 3D nanofibers network efficiently overcome the tendencies to expand and shrink during the charge-discharge processes, providing high stability to the capacitor device.⁶¹



Figure 17. (A) Optical images of the PANi/SA hydrogels formation and mechanical stability. PANi/SA hydrogels showed excellent mechanical strength, samples maintained intact shapes even under a pressure of 200 g weight. (B) Schematic illustration of hydrogen bond and van der Waals interactions within the PANi-SA polymeric chains. The synergy of the two interactions led to an increase in the hydrogel strength. Reprinted from ref. 61. Copyright © 2014 Royal Chemical Society.

CP-based flexible supercapacitors are among the most potential materials for energy storage devices due to their high redox active-specific capacitance and inherent elastic polymeric nature. There are several papers devoted to the study of flexible solid-state supercapacitors with enhanced electrochemical performance made of CPs combined with synthetic hydrogels, like PVA and phytic acid,^{62,63} or graphene oxide.⁶⁴

Within this context, Kaskel and co-workers⁶⁵ recently reported an extraordinary stretchable PANi-containing supercapacitor with high capacitance retention (up to 92%) and remarkable cycling stability (up to 35000 cycles at a high current density of 8 A g^{-1}). It is worth noting that the capacitance of previously reported PANi-based supercapacitors decreased by 70-50% over 1000 cycles, which was attributed to swelling and shrinking of the CP during charge and discharge processes, respectively. Although the innovative system described by Kaskel and co-workers⁶⁵ was not fully bio-based, it represented an important advance in the combination of biopolymer and synthetic polymer for the assembly of highly capacitive polymer electrodes. The biopolymer they chose for the hydrogel was α -cyclodextrin (α CD), a cyclic polysaccharide that contains six glucose units attached end-to-end via α -1,4 linkages. α CD presents a characteristic “micro heterogeneous environment” with a hydrophobic cavity and a hydrophilic exterior. In order to improve the mechanical integrity, these authors used polyacrylamide (PAAm), which was crosslinked with *N,N'*-methylenebis(acrylamide) and PANi. The whole system, called α CD-PAAm-PANi, was directly employed as formed, without the need of any binders (Figure 18).

Structure-property relationships

The selection of an appropriate electrolyte and electrode material is fundamental to improve the performance of energy storage devices. Considering the electrode fabrication, the most common form of electrode material for EDLC is activated carbon and its variety forms.²¹ The electrode must have high surface area, low electrical resistance, good polarizability and controllable pore size. With polymer-derived carbon electrodes, the porosity is one of the critical parameters to be controlled and the activation process is expensive. With hydrogels the porosity can be achieved by simple choosing a suitable biopolymer or modulating its processing. Additionally, larger surface areas are better achieved with hydrogels than with carbon-activated materials, just due to the easier preparation step of the first. However, hydrogels must be converted into conducting materials with semiconducting particles, like oxide metals^{37,42,43}, or with the incorporation of conducting polymers.^{58,65}

Besides ion diffusion, oxidative stability also affects the electrode's performance. Control of hydrogel porous density and ion transport inside, either with conductive nanoparticles or with electroactive polymers, is particularly important because it influences the fraction of electrode material, that is electrochemically accessible; and subsequently the capacity, energy, and power of EDLC devices. In this way, the dispersion of the conductive part with the biopolymer and the micro-morphology obtained play an important role.

Several works have evidenced that 3D porous structures are better than 3D compact biopolymer films. Comparing electrochemical performance results obtained from cellulose derivatives and sodium alginate, the late present more ordered structure, regular distribution of porosity, and is able to accommodate conductive particles with good dispersability inside the polymer matrix. The dispersability is highly dependent on the chemical interactions in the hybrid material. Yang and co-workers⁶¹ specially described the beneficial intra/inter hydrogen bond interactions between the polar groups of sodium alginate with -NH groups from polyaniline monomer units. The same observation was done by Kaskel and co-workers⁶⁵, whom have employed α -cyclodextrin as hydrogel and PANi as conductive network for flexible SCs. Controlled porosity and excellent hydrogel-conducting intramolecular interactions can increase the electrode's specific capacitance (which has a basis of mass), and the energy density (which has a basis of volume). Therefore, it is important to design an electrode's porosity to suit a particular application's needs.

With respect to the electrolyte media in SCs and batteries cells, the importance of micro- and mesoporosity obtained with biopolymers is still to be resolved. Besides, a major research is necessary to understand the relationship between electrode porosity and electrolyte interfaces.

In our recent work⁵⁸, we compared the effectivity of sodium alginate, κ -Carrageenan, chitosan and gelatin hydrogels as electrolytic media. κ -Carrageenan hydrogel exhibited a good supercapacitor response in terms of specific capacitance and cycling stability. Both SA and κ C presented fibrillar structures, homogenously distributed porous and charge transfer capability. Nevertheless, κ C fibers are more robust than SA fibers (Figure S4, in reference 58); resulting in a 3D porous structure perfectly interconnected among fibers. Low crystallinity and more brittle structure in SA hydrogel compared to the flexible and mechanically stable electrolyte obtained with κ C hydrogel led to a better electrochemical response with the late than the first, despite oxidative stability was similar in both cases.

Thus, in addition to morphology and complex intra/intermolecular interactions, anisotropy and crystallinity of biopolymers will strongly affect properties, like charge mobility and charge-discharge efficiency in SCs and secondary battery devices.

Conclusion and outlook

This review compiles the recent advances in supercapacitors and battery science and technology based on biohydrogel materials. The selection of articles reflects a combination of what is seen as impactful, opening up new directions, or providing deep and important insights.

Conductive, flexible and mechanically stable biohydrogels are the most promising candidates to replace metal inorganic and ceramic electrical storage devices. From the viewpoint of material design, there are various possible combinations of gel electrolytes and electrodes to improve the energy storage and power density performances. Among of different types of biopolymers, cellulose derivatives (HEC, BC, cellulose nanocrystals and cellulose nanofibrils) seem to have the character of compactness, lightweight nature, high strength and biocompatibility; for supercapacitor and secondary battery fabrication. Nowadays, it represents a sustainable route towards the large-scale use of energy storage devices (portable battery for mobile phone, power for household appliances, electric cars, etc.) because it can be extracted directly or eventually synthesized from biomass or recycled through paper waste; simplifying the cycle life of rechargeable batteries and supercapacitors.

Other interesting approach is the combination of biohydrogels with inherently conducting polymers. Both materials retain their unique responsive properties in the final product. This perspective has described the synchronization of various remarkable characteristics of 3D nanostructured CP-bio-hydrogels such as excellent conductivity, biocompatibility, processability and mechanical flexibility for obtaining electrolyte and electrode materials.

However, considering that a conventional inorganic battery has a typical discharge time of 0.3–3 h, specific energy of up to 230 Wh kg⁻¹, specific power up to 1500 W kg⁻¹, and cycle life of 500–2000; the effort to improve the overall energy and storage parameters using biopolymer systems is still ongoing. The research community at large clearly recognizes the need to push new advances in these topics by building on current research. Fortunately, it is an exciting opportunity to continue investigating in this direction.

Acknowledgements

This work has been supported by MICINN and FEDER funds (MAT2015-69367-R) and by DFG (DI 1748/3-1). E.A. acknowledges the Ministry of Education, Culture and Sports of Spain for a research mobility grant (PRX14/00627). Support for the research of C.A. was received through the award "ICREA Academia" for excellence in research funded by the Generalitat de Catalunya. D.D.D. thanks the DFG for the Heisenberg professorship award.

References

- 1 A. M. Kushner and Z. Guan, *Angew. Chem. Int. Ed.*, 2011, **50**, 9026.
- 2 A. Sivashanmugam, R. Arun Kumar, M. Vishnu Priya, Shantikumar V. Nair and R. Jayakumar, *Eur. Polym. J.*, 2015, DOI: 10.1016/j.eurpolymj.2015.05.014.
- 3 J. A. Hunt, R. Chen, T. van Veen and N. Bryan, *J. Mater. Chem. B*, 2014, **2**, 5319.
- 4 F. Zhao, M. L. Ma and B. Xu, *Chem. Soc. Rev.*, 2009, **38**, 883.
- 5 J. Li, Y. Kuang, Y. Gao, X. Du, J. Shi and B. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 542.
- 6 A. Vashist, A. Vashist, Y. K. Gupta and S. Ahmad, *J. Mater. Chem. B*, 2014, **2**, 147.
- 7 H. J. Schneider and R.M. Strongin, *Acc. Chem. Res.*, 2009, **42**, 1489.
- 8 L. Ionov, *Adv. Funct. Mater.*, 2013, **23**, 4555.
- 9 E. Ye, P. L. Chee, A. Prasad, X. Fang, C. Owh, V. Jing J. Yeo and X. J. Loh, *Mater. Today*, 2014, **17**, 194.
- 10 H.-P. Cong, P. Wang and S.-H. Yu, *Chem. Mater.*, 2013, **25**, 3357.
- 11 M. D. Golinska, M. K. Wlodarczyk-Biegun, M. W. T. Werten, M. A. C. Stuart, F. A. de Wolf and R. de Vries, *Biomacromolecules*, 2014, **15**, 699.
- 12 D. Morales, E. Palleau, M. D. Dickey and O. D. Velev, *Soft Matter*, 2014, **10**, 1337.
- 13 H. A. Al-Mohsin, K. P. Mineart and R. J. Spontak, *Adv. Energy Mater.*, 2015, **5**, 1401941.
- 14 L. Li, Z. Wu, S. Yuan and X-B. Zhang, *Energy Environ. Sci.*, 2014, **7**, 2101.
- 15 J. Yan, Q. Wang, T. Wei and Z. Fan, *Adv. Energy Mater.*, 2014, **4**, 1300816.
- 16 X-L. Wu and A-W. Xu, *J. Mater. Chem. A*, 2014, **2**, 4852.
- 17 N. A. Choudhury, S. Sampath and A. K. Shukla, *Energy Environ. Sci.*, 2009, **2**, 55.
- 18 T. Billiet, E. Gevaert, T. De Schryver, M. Cornelissen and P. Dubruel, *Biomaterials*, 2014, **35**, 49.
- 19 S. E. Bakarich, R. Gorkin III, M. in het Panhuis and G. M. Spinks, *Macromol. Rapid Commun.*, 2015, **36**, 1211.
- 20 M. Winter and R. J. Brodd, *Chem. Rev.*, 2004, **104**, 4245.
- 21 P. J. Hall, M. Mirzaeian, I. Fletcher, F. B. Sillars, A. J. R. Rennie, G. O. Shitta-Bey, G. Wilson, A. Cruden and R. Carter, *Energy Environ. Sci.*, 2010, **3**, 1238.
- 22 O. Inganäs and S. Admassie, *Adv. Mater.*, 2014, **26**, 830.
- 23 M. S. Islam and C. A. J. Fisher, *Chem. Soc. Rev.*, 2014, **43**, 185.
- 24 Y. N. Sudhakar, M. Selvakumar and D. K. Bhat, *Mat. Sci. Eng. B*, 2014, **180**, 12.
- 25 M. N. V. R. Kumar, *React. Funct. Polym.*, 2000, **46**, 1.
- 26 J. L. Arias and M. S. Fernández, *Chem. Rev.*, 2008, **108**, 4475.
- 27 W. Suginta, P. Khunkaewla and A. Schulte, *Chem. Rev.*, 2013, **113**, 5458.
- 28 Chitosan-based hydrogels: Functions and applications; K. Yao, J. Li, F. Yao and Y. Yin, Eds.; CRC Press, Taylor & Francis Group, Boca Raton, USA, 2011.
- 29 Chitin and chitosan derivatives: Advances in drug discovery and developments; S. K. Kim, Ed.; CRC Press, Boca Raton, FL, 2013.
- 30 L. Arof, R. H. Y. Subban and S. Radhakrishna, in *Polymer and Other Advanced Materials: Emerging Technologies and Business*, P.N. Prasad, Ed.; Plenum Press, New York, 1995, p. 539.
- 31 N. A. Choudhury, P. W. C. Northrop, A. C. Crothers, S. Jain and V. R. Subramanian, *J. Appl. Electrochem.*, 2012, **42**, 935.
- 32 N. A. Choudhury, J. Ma and Y. Sahai, *J. Power Sources*, 2012, **210**, 358.
- 33 S. Li, D. Huang, B. Zhang, X. Xu, M. Wang, G. Yang and Y. Shen, *Adv. Energy Mater.*, 2014, **4**, 1.
- 34 Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang and X. Duan, *ACS Nano*, 2013, **7**, 4042.
- 35 S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, Y. Dinga and G. Wu, *Green Chem.*, 2006, **8**, 325.
- 36 W. Zhao, L. Glavas, K. Odellius, U. Edlund and A-C. Albertsson, *Chem. Mater.*, 2014, **26**, 4265.
- 37 M. Rosi, F. Iskandar, M. Abdullah and K. Khairurrijal, *Int. J. Electrochem. Sci.*, 2014, **9**, 4251.
- 38 S. Sampath, N. A. Choudhury and A. K. Shukla, *J. Chem. Sci.*, 2009, **121**, 727.
- 39 W. Dmowski, T. Egami, K. E. Swider-Lyons, C. T. Love and D. R. Rolison, *J. Phys. Chem. B*, 2002, **106**, 12677.
- 40 W. Czaja, D. Romanovicz, R. M., *Cellulose*, 2004, **11**, 403.
- 41 Z. Schnepf, *Angew. Chem. Int. Ed.*, 2013, **52**, 1096.
- 42 H. H. Wang, E. W. Zhu, J. Z. Yang, P. P. Zhou, D. P. Sun and W. H. Tang, *J. Phys. Chem. C*, 2012, **116**, 13013.
- 43 H. H. Wang, L. Y. Bian, P. P. Zhou, J. Tang and W. H. Tang, *J. Mater. Chem. A*, 2013, **1**, 578.
- 44 C. Wang, H. Wu, Z. Chen, M. T. McDowell, Y. Cui and Z. Bao, *Nat. Chem.*, 2013, **5**, 1042.
- 45 I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov and G. Yushin, *Science*, 2011, **334**, 75.
- 46 W. G. Moon, G-P. Kim, M. Lee, H. D. Song and J. Yi, *ACS Appl. Mater. Interfaces*, 2015, **7**, 3503.
- 47 M. Tako, S. Nakamura, *Carbohydr. Res.*, 1988, **180**, 277.
- 48 M. Wahid, G. Parte, R. Fernandes, D. Kothari and S. Ogale, *RSC Adv.*, 2015, **5**, 51382.
- 49 Handbook of battery materials, C. Daniel and J. O. Besenhard, Eds.; 2nd Edition, Wiley-VCH, Weinheim, Germany, 2011.
- 50 N. A. Choudhury, S. Sampath and A. K. Shukla, *J. Electrochem. Soc.*, 2008, **155**, A74–A81.
- 51 J. B. Lee, S. Peng, D. Yang, Y. H. Roh, H. Funabashi, N. Park, E. J. Rice, L. Chen, R. Long, M. Wu and D. Luo, *Nat. Nanotechnol.*, 2012, **7**, 816.

- 52 J. Hur, K. Im, S. Hwang, B. Choi, S. Kim, S. Hwang and N. Park, *K. Kim. Sci. Rep.*, 2013, **3**, 1.
- 53 J. Hur, K. Im, S. W. Kim, U. J. Kim, J. Lee, S. Hwang, J. Song, S. Kim, S. Hwanga and N. Park, *J. Mater. Chem. A*, 2013, **1**, 14460.
- 54 L. Pan, G. Yu, D. Zhai, H. R. Lee, W. Zhao, N. Liu, H. Wang, B. C.-K. Tee, Y. Shi, Y. Cui and Z. Bao, *Proc. Natl. Acad. Sci. USA*, 2012, **109**, 9287.
- 55 Y. Zhao, B. Liu, L. Pan and G. Yu, *Energy Environ. Sci.*, 2013, **6**, 2856.
- 56 H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao and Y. Cui, *Nat. Commun.*, 2013, **4**, 1943.
- 57 L. Chen, Y. Chen, J. Wu, J. Wang, H. Bai and L. Li, *J. Mater. Chem. A*, 2014, **2**, 10526.
- 58 M. M. Pérez-Madrigal, F. Estrany, E. Armelin, D. Díaz Díaz, C. Alemán, *J. Mater. Chem. A*, 2016, **4**, 1792.
- 59 W. Hu, S. Chen, Z. Yang, L. Liu and H. Wang, *J. Phys. Chem. B*, 2011, **115**, 8453.
- 60 Y. Li, X. Zhao, Q. Xu, Q. Zhang and D. Chen, *Langmuir*, 2011, **27**, 6458.
- 61 H. Huang, X. Zeng, W. Li, H. Wang, Q. Wang and Y. Yang, *J. Mater. Chem. A*, 2014, **2**, 16516.
- 62 Y. Shi, L. Pan, B. Liu, Y. Wang, Y. Cui, Z. Bao and G. Yu, *J. Mater. Chem. A*, 2014, **2**, 6086.
- 63 K. Wang, X. Zhang, C. Li, H. Zhang, X. Sun, N. Xu and Y. Ma, *J. Mater. Chem. A*, 2014, **2**, 19726.
- 64 I. Shown, A. Ganguly, L-C. Chen and K-H. Chen, *Energy Sci. Eng.*, 2015, **3**, 2.
- 65 G-P. Hao, F. Hippauf, M. Oschatz, F. M. Wisser, A. Leifert, W. Nickel, N. Mohamed-Noriega, Z. Zheng and S. Kaskel, *ACS Nano*, 2014, **8**, 7138.