

Sustainable Modification of Chitosan Binder for Capacitive Electrodes Operating in Aqueous Electrolytes

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Biopolymers emerged in recent years as a promising alternative for a more sustainable manufacturing of electrochemical energy storage systems. In fact, for environmentally friendly aqueous systems, fluorinated polymers are usually adopted. For this reason, substituting these polymers with water processable

binders could improve the overall environmental impact of the device. In this study, a low – cost and environmentally friendly modification of chitosan binder for self-standing activated carbon electrodes operating in Na ion, aqueous electrochemical double layer capacitors is reported and discussed.

Introduction

The energetic transition from fossil – based energy sources towards renewable energy technologies have brought a strong need for energy storage materials for efficient, long – lived, and safe energy storage devices, to support their discontinuous energy production.^[1] The electrochemical energy storage systems (EESS) have been demonstrated to be the most versatile to this purpose, meeting the requirements of high level of safety, low cost, low maintenance, and long cycle life.^[2–4]

EESS could be classified by their different energy storage mechanisms. While metal ion batteries deliver high energy density by faradaic processes and metal ion intercalation, electrochemical double layer supercapacitors (EDLC) provide high power and excellent cycling stability based on capacitive processes via the formation of an electrochemical double layer.^[5,6]

Up to now organic electrolytes have been commonly used in supercapacitors, thanks to a wide electrochemical stability window, up to 3.5 V, enabling high energy density. However, despite a narrow operating voltage window, aqueous electrolytes represent one of the most currently studied and developed technology, featuring high ionic conductivity, low cost and environmental compatibility.^[7–9]

Specifically, aqueous Na ion based EDLCs satisfy both safety and cost requirements by using water as solvent and sodium as the cation of low – cost electrolytes.^[10,11] Furthermore, aqueous processes involving water soluble binders could improve the overall sustainability and decrease the production costs of the device as well, compared to conventional processes that make use of fluorinated polymers.^[12–16]

Many of the water processable binders originate from renewable sources and are biodegradable, like cellulose, alginate, starch, etc., and are viable candidates for substitute fluorinated polymers both in supercapacitors and batteries.^[2,17–21]

Some of these binders are already successfully used in Li ion batteries with organic electrolytes,^[22–27] and in aqueous Zn batteries.^[28,29]

However, the use of water-soluble biopolymers, is not feasible in most of the aqueous electrolytes, because of a progressive electrode disruption following binder dissolution.

Chitosan, reported in Figure 1, is a linear polysaccharide composed of randomly distributed β -(1 \rightarrow 4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit), extracted from crustacean shells and some fungi, which is already used in non-aqueous Li ion batteries.^[25,27,30]

We recently demonstrated that crosslinked chitosan with N-(3-dimethylaminopropyl)-N'-ethyl carbodiimide (EDC) could be used as binder for different electrode materials operating in aqueous electrolytes.^[31] EDC is generally used, in biochemistry, to form amide bonds for the immobilization of large biomolecules. However, it is not a very health – friendly molecule, and for this reason here we present a novel, more sustainable and

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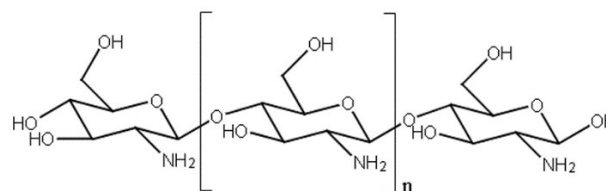


Figure 1. Chemical structure of chitosan.

less expensive chemical modification of chitosan with maleic anhydride (MA). Moreover, as an added value, MA can also be obtained from renewable sources by microbial fermentation of biomass.^[32,33] The reaction of chitosan with MA assures a flexible and robust structure to self-standing activated carbon (AC) electrodes, stable even in aqueous EDLCs. Also, the absence of current collectors in self-standing electrodes, which is valuable in terms of use of raw materials, cost, and device weight and volume, is an important feature in view of increasing the overall sustainability of the device. This concept can also be extended to other aqueous systems such as Na ion batteries.

Results and Discussion

Chitosan is almost insoluble in pure water and in most organic solvents because of strong intermolecular and intramolecular hydrogen bonding interactions.^[31,34] It dissolves in slightly acidic environment, at pH values below 6.5. Diluted aqueous solutions of carboxylic acids could dissolve chitosan, because of "proton exchange" interaction between $-\text{COOH}$ of the organic acids and $-\text{NH}_2$ groups of chitosan.^[31,34,35] Thus, acetic acid was chosen as a viable proton donor able to dissolve chitosan.^[36–38]

MA was selected as acetylating agent. The addition of MA to dissolved chitosan, led to a modification of the amino groups of chitosan to amides.

According to the proposed reaction in Figure 2, following ring opening of MA, the lone pair at the nitrogen atom of amines in chitosan chain interacts with the carbonyl of MA leading to the formation of amide. MA can also react with $-\text{CH}_2\text{OH}$ group with the release of a water molecule. The

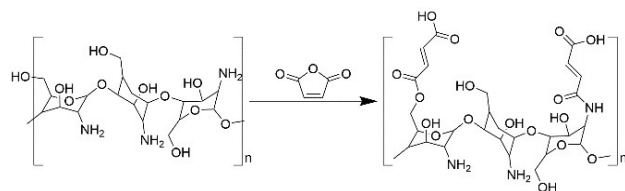


Figure 2. Scheme of chitosan modification with maleic anhydride.

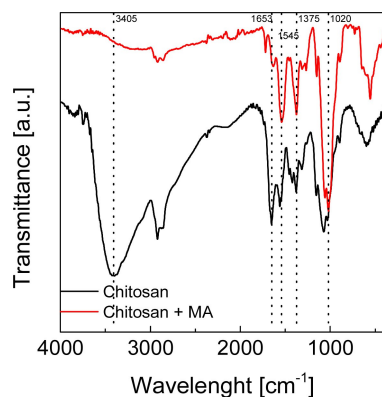


Figure 3. FTIR-ATR spectra of chitosan and modified chitosan with maleic anhydride, with 64 scans performed from 4000 to 400 cm^{-1} .

obtained polymer results insoluble in water because of the increased amount of less polar moieties in the main chain, and electrodes prepared with this modified binder show high stability in water (Figure S1).

Figure 3 shows the Fourier transform infrared spectroscopy – attenuated total reflection (FTIR – ATR) spectra of pure chitosan and of chitosan upon interaction with MA (modified chitosan).

There are no significant differences in the two spectra but in the region around 3400 cm^{-1} , corresponding to primary amine and alcohol stretching signals that are nearly absent in the modified chitosan. Absorption in 1653 cm^{-1} and 1545 cm^{-1} are compatible with asymmetric N–H bending of amines and asymmetric stretching in amides respectively. The peaks around 1030 cm^{-1} corresponds to C=O stretching in acetamide. The other signals observed in the modified chitosan spectrum were similar to the native chitosan, especially looking at the intensity of the signals around 2800 cm^{-1} corresponding to aliphatic C–H stretching, demonstrating that modification with MA does not affect the polymer backbone.

Thermogravimetric analysis (TGA) curves for the chitosan and modified chitosan are reported in Figure 4. Although both samples were dried, modified chitosan demonstrated a lower amount of residual water, as it could be seen from the lower mass decrease below 150°C . Compared to chitosan, the degradation of the modified polymer occurs in a wide interval of temperatures. The addition of MA causes a shift on the beginning of thermal degradation at lower temperatures, around 160°C , due to decomposition of high volatile fractions originated by side chains. The latter are primary degradation sites upon the polymer backbone. However, the degradation profile appears less steep compared to that of chitosan, because of the longer side chain formed after MA addition.

The morphology of the free-standing AC electrodes, prepared as described in the experimental section, was evaluated through scanning electron microscopy (SEM). In SEM images of pristine AC electrodes (Figure S2) no evident inhomogeneity and cracks were observed. We also performed porosimetric analysis of the carbon powder and of electrodes made with pure chitosan and electrodes with chitosan modified

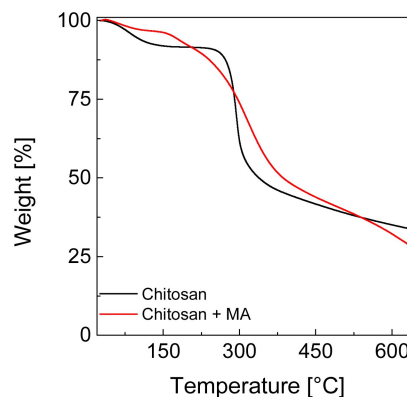


Figure 4. TGA curves of chitosan and modified chitosan with maleic anhydride, performed in Ar atmosphere, $10^\circ\text{C min}^{-1}$ ramp up to 650°C .

with maleic anhydride to compare the amount of the surface area blocked by the two binders. The isotherms of the three samples, shown in Figure 5a, evidence a high microporous contribution as well as a mesoporous one. Table 1 reports the surface area of AC powder and electrodes with different binders, estimated by BET, BJH and DFT models. The BET surface area is quite high for all samples, with an obvious decrease in passing from the powder to the electrodes. However, the BET area takes also into account micropores that could be less involved in the electrochemical process occurring at the electrode. BJH surface area, evaluated in the range of pore size from 1 to 400 nm, displays lower values, and even lower values resulted from DFT analysis in the range 1.5–234 nm. Surface area of electrodes with chitosan and MA-modified chitosan are not significantly different, with the latter slightly higher, and are ca. 30% lower than that of AC powder.

MA-modified chitosan was the binder of the working and counter electrodes for impedance and galvanostatic charge and

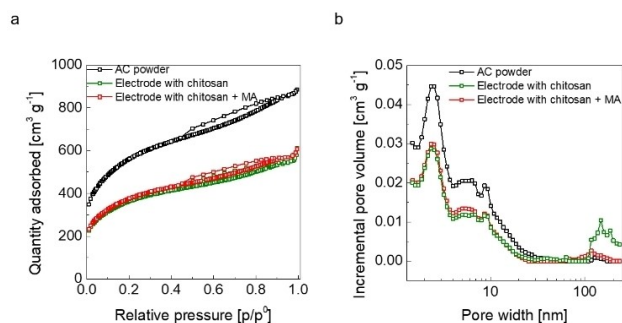


Figure 5. (a) Nitrogen adsorption–desorption isotherms of AC powder, electrode with chitosan binder, and electrode with MA-modified chitosan; (b) incremental pore volume vs. pore diameter size of AC powder, electrode with chitosan binder, and electrode with MA-modified chitosan binder

Surface area [m ² g ⁻¹]	AC powder	Electrode with chitosan	Electrode with chitosan + MA
BET	1972	1277	1316
BJH (1.0–400.0 nm pores)	920	579	619
DFT (1.5–234.0 nm pores)	510	330	350

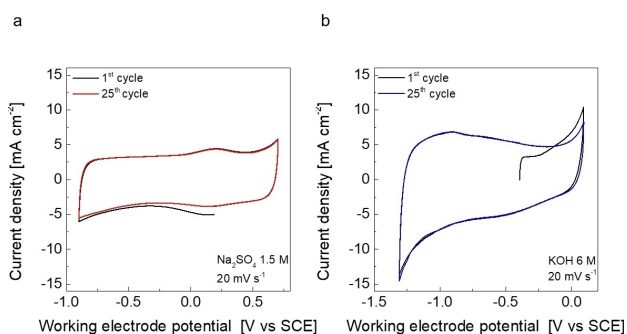
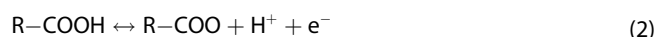
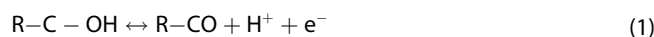


Figure 6. (a) CVs of AC electrodes with MA-modified chitosan binder at 20 mV s⁻¹ in Na₂SO₄ 1.5 M and (b) and in KOH 6 M.

discharge measurements, and polytetrafluoroethylene (PTFE) aqueous suspension was used as binder for the counter-electrode used in cyclic voltammetry measurements. The electrochemical tests were performed in Na₂SO₄ 1.5 M aqueous solutions and, for comparison, in KOH 6 M, a typical aqueous electrolyte used in EDLCs.

The cyclic voltammeteries (CVs) of these electrodes, reported in Figure 6, display a typical capacitive behaviour, with well-defined box shaped cycles. Electrode materials demonstrated stable cycles in Na₂SO₄ electrolyte in the range –0.9 V to 0.7 V (1.6 V), which is a good result for conventional aqueous electrolytes.^[39–41] For comparison, the electrochemical window of KOH electrolyte was narrower, 1.1–1.2 V. In the CVs performed in Na₂SO₄ broad oxidation peaks around 0.21 V and reduction peaks 0.15 V are perceptible, indicating the occurrence of a faradaic reaction.

This peak could be attributed to redox processes taking place at the carbon electrode surface, involving oxygen-containing groups e.g., alcohol and carboxylic acids, according to equation (1) and (2):^[42–44]



These functional groups are formed during the activation process of porous carbon, and therefore can be reversibly oxidized and reduced especially in acidic and neutral environment. The faradaic contribution to the total capacitance was estimated to be less than 4%.

Figure 7 shows the Nyquist plots for symmetrical cells with AC electrodes with Na₂SO₄ and KOH electrolytes, recorded in three electrode mode after cell assembly (*t*₀) and after 50 cycles

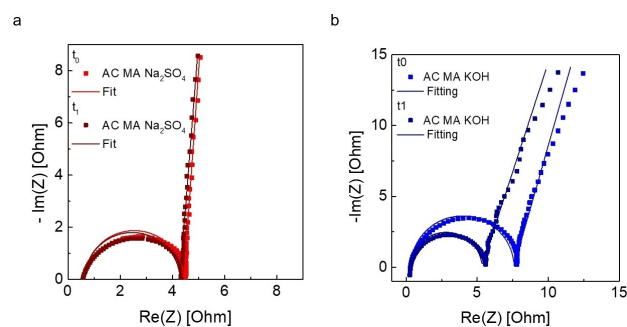


Figure 7. Nyquist plots of EIS spectra and fitting curves of AC electrodes (a) in Na₂SO₄ 1.5 M and (b) KOH 6 M recorded after cell assembly (*t*₀) and after 50 cycles at 0.5 A g⁻¹ (*t*₁). Frequency range 100 kHz–0.1 Hz, 20 points per decade, ±5 mV amplitude.

at 0.5 A g^{-1} (t_1). Fitting curves were obtained using the equivalent circuit $R_1(R_2/Q_2)Q_3$ displayed in Figure S3, where R_1 is the electrolyte resistance, R_2/Q_2 represent the resistance and the capacitance (as constant phase element, CPE) in parallel, related to the charge transfer of the faradaic process, and Q_3 is the CPE attributed to the double layer of a non-ideal capacitor, visible as a line with angles $< 90^\circ$ with respect to X axis.

It is possible to identify the electrolyte resistance (R_s) as the point at the highest frequency, the semicircle due to the charge transfer resistance and the related double layer capacitance, and an almost linear part ascribed to the non-ideal double layer capacitance of the electrode, with the intercept with the X-axis providing an indication of the total resistance of the electrode (equivalent series resistance, ESR).

Table S1 lists the parameters of the equivalent circuit obtained from the fitting. The results of the fitted spectra show higher electrolyte resistance of the cell with Na_2SO_4 than of the cell with KOH, in agree with the conductivity values shown in Table S2. The electrode with MA – modified chitosan in Na_2SO_4 (Figure 7a) shows smaller charge transfer resistance (R_2) than in KOH, which does not vary after 50 cycles. The impedance spectra were fitted, by Q_3 in the low frequency region. The straight lines with angles near 90° were ascribed to the double layer of a non-ideal capacitor. The Table also displays the data of ESR evaluated by EIS and galvanostatic charge discharge (GCD) cycles at 0.5 mA cm^{-2} . The values of the ESR from the two techniques are in good agreement. The ESR value of the electrode in KOH is slightly higher, probably due to a non-complete wetting of the electrode. The decrease of ESR value over cycling confirms our hypothesis.

Resistances values obtained from our electrodes are good and comparable with other results reported in literature.^[45] It is worth mentioning that self-standing electrodes directly placed on the stainless-steel collector of the cell may suffer of poor contact, contrarily to the electrode in which the current collector provides a uniform contact between the electrode material and the cell terminal. Nevertheless, in Na_2SO_4 MA – modified chitosan electrodes show lower resistance values compared to the electrodes modified with EDC (ca. 20–27 ohm, Figure S4).

The electrochemical behaviour of chitosan-modified AC electrodes was evaluated in Na_2SO_4 and KOH electrolytes by GCD at different current densities in three electrodes symmetrical cells. We performed the tests in triplicate, and the mean capacitance and capacitance retention are reported in the Table S3 as Supplementary Materials. In Figure 8 are reported the results of the best performing electrodes.

Capacitance values, shown in Figure 8, are quite interesting for activated carbon electrodes operating in aqueous EDLCs,^[41,46–49] exhibiting initial capacitance values above 145 F g^{-1} and 110 F g^{-1} in Na_2SO_4 and KOH, respectively, at the lowest specific current. These values are significantly higher than those obtained with AC electrodes featuring EDC-cross-linked chitosan, reported in Figure S5. Despite the better ionic conductivity of KOH, listed in Table S2, capacitance values obtained in Na_2SO_4 are higher at each specific current. This is probably attributed to the electrostatic repulsion between OH^-

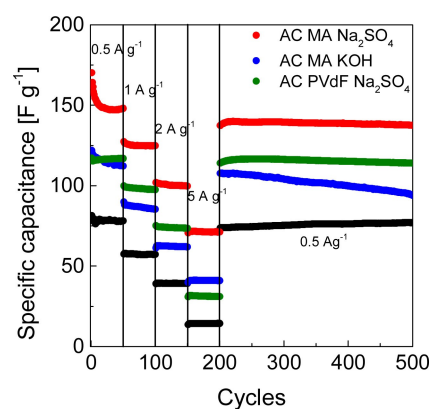


Figure 8. Specific capacitance values recorded at different specific currents of AC electrodes in Na_2SO_4 1.5 M (red circles), KOH 6 M (blue circles), and AC electrodes with PVdF binder in Na_2SO_4 1.5 M (green circles).

and the deprotonated oxygen containing groups, $-\text{COO}^-$ and $-\text{RO}^-$ on the activated carbon surface, that hinder the formation of the double layer.^[50,51]

Figure 8 also reports the capacitance values of an electrode with PVdF as binder. Despite the good stability in aqueous electrolyte, the electrodes with PVdF exhibited lower specific capacitance than electrodes with MA – modified chitosan as binder. Lower values could be explained by the higher hydrophobic behaviour of PVdF binder that doesn't enable a good wetting of the microporosity of active material.

After 200 cycles, AC electrodes recovered almost the initial capacitance values at 0.5 A g^{-1} and remained stable for over 500 cycles in Na_2SO_4 , while capacitance values in KOH suffered a steady decrease, approaching values close to chitosan cross-linked with EDC electrode (Figure S5). This phenomenon may be attributed to the water reaction, given that the charge/discharge cycles were carried out in the maximum voltage window of 1.2 V.

In the initial cycles, AC electrode in KOH shows higher efficiency values, reported in Figure 9, and reached values close to 99%. AC electrodes in Na_2SO_4 , shows lower initial values that stabilize after fifty cycles reaching comparable values. The

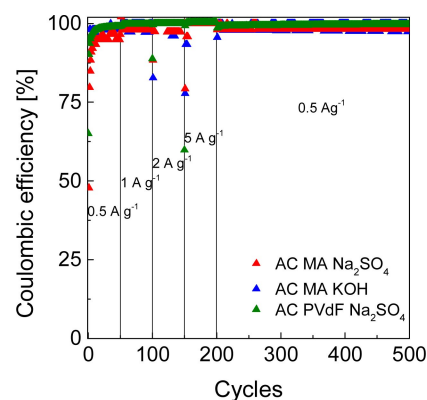


Figure 9. Coulombic efficiency values recorded at different specific currents for AC electrodes in Na_2SO_4 1.5 M (red triangles), KOH 6 M (blue triangles) and AC with PVdF binder in Na_2SO_4 1.5 M (green triangles).

differences in the coulombic efficiencies of the initial cycles are attributed to the different bulkiness of the SO_4^{2-} ion with respect to OH^- . Sulphates ions attachment to the surface or penetration into the pores vary with surface impurities and may not remain the same after several charge-discharge cycles.^[52,53]

The AC electrodes with MA – modified chitosan binder demonstrated stable in aqueous environment, capable of operating either at low and high specific current, as visible from the typical triangular profile of charge and discharge cycles in Figure 10.

Nevertheless, charge and discharge profiles are not perfectly straight but appears slightly bended, because of the different double layer formation process, involving ions stored and released close to electrode surface, with less hindrance, and ions contained in the inner pore structure of the electrode.

The electrochemical stability of the electrodes with modified chitosan binder upon prolonged cycling at 0.5 A g^{-1} in Na_2SO_4 is shown in Figure 11. The tests were carried out in triplicate and the average values of specific capacitance and capacitance retention were approximately $141 \pm 9 \text{ F g}^{-1}$, and $89 \pm 4 \%$ respectively. The reported results are those of the best performing electrodes. After the initial 700 cycles, electrodes demonstrated quite stable, reaching a final value of 93.4% capacitance retention after 5000 cycles.

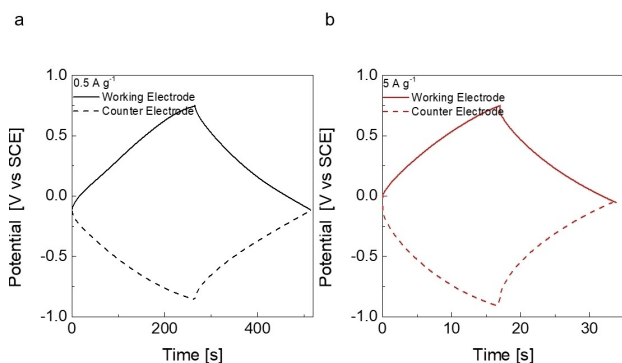


Figure 10. Potential profiles of the positive and negative AC electrodes with MA – modified chitosan binder during GCD cycles (a) in Na_2SO_4 1.5 M at 0.5 A g^{-1} (black line) and (b) 5 A g^{-1} (red line).

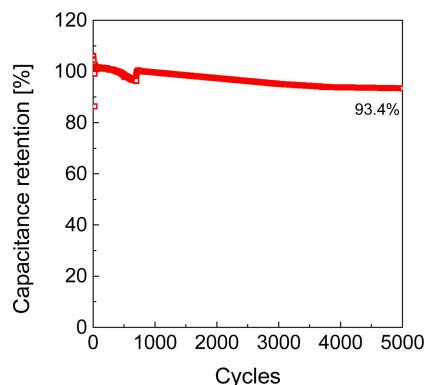


Figure 11. Capacitance retention of AC electrode with MA-modified chitosan binder in Na_2SO_4 1.5 M over GCD cycles at 0.5 A g^{-1} .

Finally, we evaluate the possibility to easily recover the electrode material, even if it is simply carbon, by dissolving the electrode in the same solution of 1 vol.% acetic acid used for chitosan dissolution during electrode preparation.

After 16 hours of immersion in 10 mL of solution, the electrode was sonicated for 30 minutes at 40°C . The suspension of the electrode material (activated and conductive carbon), visible in Figures S6, was centrifuged at 5000 rpm for 5 minutes. The powder was then dried in oven at 60°C overnight and weighed. Nearly 70% of the carbonaceous materials has been recovered, demonstrating, in addition to the sustainability of this approach, also its suitability in the frame of circular economy.

Conclusion

In this work we evaluated a cheap and sustainable modification of chitosan binder with maleic anhydride, resulting in a water insoluble binder for electrochemical devices operating in aqueous media. Specifically, carbon electrodes for double layer capacitors have been investigated, although this approach is suitable also for other electrochemical devices. As a matter of fact, electrodes with MA-modified chitosan binder demonstrated lower resistances and higher electrochemical performance compared to electrodes with chitosan binder modified with EDC. Electrodes with MA-modified chitosan exhibited 99% coulombic efficiency at different specific currents, and ca. 140 F g^{-1} specific capacitance at 0.5 A g^{-1} . These electrodes showed good stability over 5000 cycles, with a capacitance retention of ca. 90%. The feasibility of MA-modified chitosan binder for electrodes working in aqueous systems has been demonstrated, as well as the possibility of an easy and environmentally friendly recycling of electrodes materials.

Experimental Section

Modified chitosan membranes were obtained by adding 54 mg chitosan (Sigma Aldrich, from shrimp shells practical grade) powder in an appropriate amount of aqueous solution of acetic acid (Carlo Erba, $\text{RPE} \geq 99.5\%$) 1 vol.% and left under stirring for one hour at room temperature, until complete dissolution. Maleic anhydride (MA, Carlo Erba, $\text{RPE} \geq 98.5\%$) was added to the viscous chitosan solution, in 1:2 molar ratio respect to chitosan, and left under stirring for 16 hours. The solution with modified chitosan was casted on a Teflon mold and left overnight at RT to allow solvent evaporation. The obtained film ($38 \mu\text{m}$ thickness) has been rinsed with acetone and water, in order to remove unreacted MA and acetic acid, respectively. A final drying of 12 hours at 80°C in oven was performed before thermogravimetric analysis (Q50 TA Instrument), where Argon was used as sample gas (60 mL/min) and balance gas (40 mL/min). Bruker Alpha spectrometer was used for Fourier transform infrared spectroscopy - attenuated total reflection (FTIR – ATR). SEM images were collected by a ZEISS EVO 50 instrument.

Self-standing electrodes were prepared as described in Figure 12. Electrodes with MA-modified chitosan were prepared by mixing in a slurry suspension 80 wt.% active material (Picacatif activated carbon, BP10, BET specific surface area $1850 \text{ m}^2 \text{ g}^{-1}$, Pica Co.),

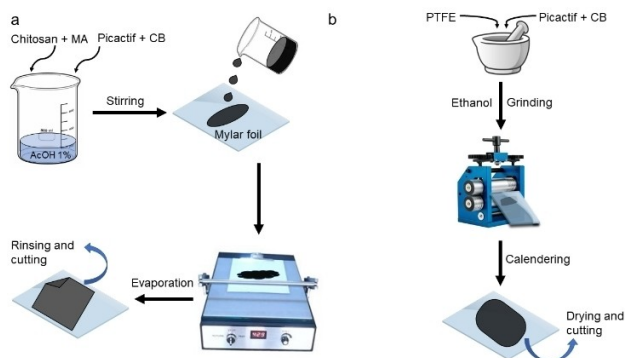


Figure 12. (a) Preparation of self-standing AC electrodes with modified chitosan, pure chitosan and PVdF binder and (b) preparation of self-standing AC electrodes with PTFE binder.

10 wt.% carbon black (CB, Super C45, Imerys) and 10 wt.% chitosan. Chitosan and MA (5.2:1 w/w), have been poured in an aqueous solution containing 1 vol.% acetic acid and kept under stirring. After complete dissolution of the binder, active material and conductive additive were added, and left under stirring overnight to homogenize the solid suspension. The slurry was roll coated on a mylar sheet, and dried at RT overnight. The electrode foil was detached from mylar substrate, and self-standing electrodes have been punched (0.636 cm²) and heat treated for 65 °C for 12 hours. The obtained electrodes had a thickness of 42 μm and a mass loading in the range of 2.5–3.0 mg cm⁻².

Crosslinked chitosan with EDC electrodes has been prepared following the procedure described in our previous work.^[31]

Electrodes with polyvinylidene fluoride (PVdF) were prepared in N-methyl pyrrolidone (NMP, Fluka, ≥99%) by mixing 80 wt.% active material, 10 wt.% carbon black, and 10 wt.% PVdF (Kynar, Arkema). Using the same procedure described for electrodes with chitosan, the electrode tape was dried at RT for 72 h. The electrodes had a thickness of 54 μm and a mass loading of 3.6–3.9 mg cm⁻².

AC electrodes with PTFE were obtained by mixing in a mortar 90 wt.% of Picactif active material, 5 wt.% CB and 5 wt.% of PTFE aqueous suspension (Dupont, 60% wt), and adding stepwise 350 μL of ethanol (Sigma Aldrich, absolute ≥99.8%). Electrode foil was laminated until a uniform thickness of 120 μm was obtained. Self-standing electrodes have been punched (0.785 cm²) and dried at 120 °C for 12 hours. These electrodes had a mass loading of 11 mg cm⁻² and therefore were used as non-limiting counter electrodes to perform CVs.

Nitrogen adsorption isotherms at 77 K of the AC powder and of the electrodes prepared with chitosan and MA – modified chitosan as binders were collected using a Micromeritic ASAP 2020 porosimeter. The samples were dried for at least 24 h at 120 °C before testing. The electrode with chitosan were prepared with the same procedure described in the experimental part without adding the maleic anhydride.

For electrode recycling, Elmasonic S – 15 H sonicator and REMI R – 8D centrifuge was used.

Electrochemical setup: Self-standing AC electrodes were characterized by cyclic voltammetry, galvanostatic charge/discharge cycles and electrochemical impedance spectroscopy by using a potentiostat/galvanostat Biologic VSP. Impedance spectra were fitted by Boukamp's E_qC software. T – shaped PTFE Bola cell (Bohlender GmbH) were used, and a silver disk was used as a pseudo reference

electrode. All the potentials were calculated vs. saturated calomel electrode (SCE).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: aqueous devices · chitosan · electrode recycling · sustainable processing · water soluble binder

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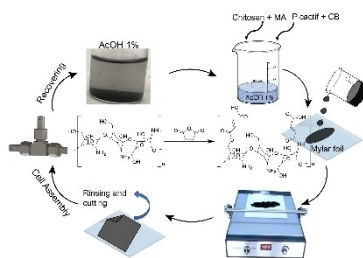
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RESEARCH ARTICLE

Chitosan Binder for Capacitive Electrodes: A cheap and sustainable modification of chitosan binder with maleic anhydride, resulting in a water insoluble binder for aqueous electrochemical devices, has been investigated. The binder was tested in capacitive carbon electrodes in aqueous media and demonstrated a good chemical and electrochemical stability.



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Sustainable Modification of Chitosan Binder for Capacitive Electrodes Operating in Aqueous Electrolytes

