



Short communication

Enabling high areal capacitance in electrochemical double layer capacitors by means of the environmentally friendly starch binder

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HIGHLIGHTS

- Potatoes starch is proposed as superior water-processable binder for electrochemical double layer capacitors.
- The presence of amylopectin provides enhanced mechanical properties and suppresses the cracking of the electrode.
- Potatoes starch enables considerably higher electrode loadings resulting on increased areal capacitance.

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ABSTRACT

Potatoes starch (PS), a natural polymer obtainable from non-edible sources, is for the first time evaluated as alternative water-processable binder for Electrochemical Double-Layer Capacitor (EDLC) electrodes. Morphological and electrochemical properties of activated carbon (AC)-based electrodes are investigated and compared to those achieved with the state-of-the-art aqueous binder (CMC, i.e. Na-carboxymethyl cellulose). The obtained results suggest substantial benefits of PS, in particular regarding the electrode fabrication process. As a matter of fact, owing to its amylopectin content (moderately branched polysaccharide), PS displays only minimal shrinkage upon drying, resulting on rather homogeneous electrodes not presenting the dramatic surface cracking observed with CMC. Furthermore, owing to the smaller volume of water required for the processing, much higher active material loading per area unit can be achieved. This is reflected on improvements of up to 60% in terms of areal capacitance.

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1. Introduction

Electrochemical energy storage devices, in particular lithium ion batteries (LIBs) and electrochemical double-layer capacitors (EDLCs), are nowadays being employed in a continuously rising number of applications. Storing energy produced via renewable sources and re-use it on demand has become today's reality while electrically powered vehicles will likely represent the normality in the very next future. This leads to a growing market for such devices, raising, at the same time, concerns about the impact their production and disposal could have on the environment. Thus, many efforts are ongoing to develop environmentally friendly devices constituted by non-toxic materials that can be safely

produced and disposed without using hazardous chemicals. A very effective approach is constituted by the use of water processable binders. Several natural (and naturally derived) polymers have been already proposed for LIBs, such as Na-carboxymethyl cellulose (CMC) [1,2], natural cellulose [3], chitosan [4], alginate [5], Xanthan Gum [6,7], etc. Besides their enhanced environmentally friendliness, more appealing is their capability to improve the cyclability of alloying anodes, by retaining the contact among particles, even when the active particles undergo severe volume expansion.

Strain associated to faradaic reactions is not an issue in EDLC electrodes, where, theoretically, the charge is simply stored in the double layer. This fact partially justifies the limited attention paid to the binder in EDLCs-related scientific literature. Nevertheless, it has been demonstrated that green binders can provide interesting benefits to EDLC as well [8–11]. Our recent work, for example, demonstrated as natural cellulose enables superior performance than PVdF under prolonged floating conditions at high cell voltages (i.e., 3.7 V for 750 h) [10]. Despite the quite appealing properties,

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natural cellulose is insoluble in water and requires slightly more complex electrode processing. From this point of view, CMC would be rather preferred. However, upon drying, it becomes very brittle resulting on electrodes which can easily crack or peel off. This phenomenon is usually attributed to the shrinkage of the linear polymeric chains upon water removal. The brittleness of CMC-based electrodes can be attenuated by introducing rubberizing agents in small amounts. Styrene butadiene rubber (SBR) is often employed to make thick electrode layers [12], which are flexible enough to be rolled or bent, depending on the cell configuration (e.g., cylindrical, prismatic, etc.). Nevertheless, the employment of SBR should be, when possible, avoided. Its low melting point (ca. 120 °C) could, indeed, hinder the proper electrode drying. CMC-based electrodes need, in fact, to be dried under vacuum at relatively high temperature (above 150 °C) to ensure the removal of water traces. Alternatively to CMC, Yamagata et al. demonstrated that alginate (a typical polysaccharide derived from brown seaweed) can be also employed as binder in EDLCs, both with organic and ionic liquid (IL) electrolytes [11]. Compared to CMC and PVdF, alginate enables higher capacitance retention at high currents by decreasing the cell resistance.

As a proof of concept, we report here the results achieved using a more appropriate polysaccharide binder for EDLCs electrodes, namely potatoes starch. Starch is, after cellulose, one of the most abundant natural polymers and it is, for the larger extent, extracted from particular kinds of non-edible potatoes. Differently from CMC, alginate and chitosan, starch is composed by two different polymers: amylose and amylopectin. Amylose, similarly to the above mentioned binders, is constituted by linear chains. Amylopectin is a moderately branched polymer instead. Depending on the extraction source the ratio between the two polysaccharides might vary. However, amylopectin is generally the main component of starches (ca. 80%) [13]. Such large content of branched polymer appears to be the key to meet the physical characteristics of commercial electrodes (e.g. thickness >100 µm; loading >5 mg cm⁻²), as demonstrated by morphological and electrochemical investigations on symmetric EDLCs. Taking CMC as term of comparison, we show the major advantages enabled by the use of starch.

2. Experimental

2.1. Electrode preparation

Composite electrodes based on activated carbon (DLC Super 30, Norit) were prepared via aqueous processing of polysaccharides-containing slurries. Commercially available starch from potatoes (high purity analytic grade, Sigma Aldrich), hereinafter called PS, was firstly dissolved in ultrapure water (milliQ) to obtain a 3.2% wt. solution. Although this specific kind of starch exhibits a rather good solubility already at RT, the solubilisation of the binder was accelerated by heating up the solution to 60 °C. It is important to notice that prior to choosing PS, preliminary tests were also conducted using starches extracted from other natural sources, such as rice and wheat. These, however, showed poorer solubility in water. Afterwards, carbon black (SuperC65, Imerys Graphite & Carbon) was added to the PS solution to form the slurry via treatment in ultrasonic bath for 30 min followed by magnetic stirring for additional 30 min. Activated carbon was then added into the slurry, which was further stirred for 1 h. Finally, the homogenous black ink was coated on pre-etched Al foil using a doctor blade coater, varying the wet coating thickness from 150 to 450 µm. The casted electrodes were then dried overnight at 80 °C. For comparison purposes, composite electrodes employing Na-carboxymethyl cellulose (CMC Walocell 2000 PA, Dow Wolff Cellulosics) as binder

were prepared following the same procedure. However, differently from PS, CMC slurries with comparable viscosities were obtained using larger volumes of water resulting on more diluted solutions, i.e. 2.6 wt.%. When evaluating the cathodic stability of PS, PVdF and natural cellulose (NC) were also considered as additional term of comparison. All experimental details about the electrode preparation with such binders are already reported in our previous publication [10].

All investigated composite electrodes were constituted by activated carbon, carbon black and binder in a weight ratio of 85:5:10. The sample morphology was studied by Scanning Electron Microscopy (SEM). Micrographs were acquired with a Carl Zeiss AURIGA equipped with a field emission electron gun and an in-lens detector. The acceleration voltage was set to 5 kV.

2.2. Electrochemical characterization

To perform electrochemical tests, electrodes were punched into disks with a diameter of 12 mm (area: 1.13 cm²). These were further dried for 12 h under vacuum at 180 °C, in order to remove any residual water trace, before being transferred in an Argon-filled glove box (LabMaster, Mbraun GmbH) with H₂O and O₂ content below 0.1 ppm. Experiments were conducted in both 2- and 3-electrode Swagelok type cells. Symmetrical EDLC were assembled using two identical composite electrodes. These were separated by glass fiber disks (GF/D, 670 µm thickness, Whatman), which were soaked with 150 µL of electrolyte. The employed electrolyte was 1 M Et₄NBF₄ in propylene carbonate (PC). The cathodic stability of the electrodes was investigated in 3-electrode cell configuration using an oversized counter electrode (composition: activated carbon, carbon black, PTFE = 85:5:10) with a ten times larger amount of active material and an Ag wire as pseudo-reference electrode. In these experiments neat N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI), synthesized in our laboratory as described elsewhere in literature [14,15], was used. Cyclic voltammetry (CV) and galvanostatic cycling (current loadings from 5 to 50 mA cm⁻²) were performed to evaluate the EDLC capacitances using a programmable multi-channel potentiostat-galvanostat (VMP3, Biologic Science Instruments). At small sweeping rates (i.e., 1 mV s⁻²), the fairly rectangular shape of the voltammetric curves allowed to estimate the areal capacitance (F cm⁻²) by simply dividing the specific current (in mA cm⁻²) by the scan rate (in mV s⁻¹). With regards to rate capability and long term stability tests, capacitance values were calculated from the slope of the discharge curve, as already described elsewhere [16]. The investigated voltage range were selected as function of the employed electrolyte (PC-based or PYR₁₄TFSI) and cell setup (2- or 3-electrode). Electrochemical impedance spectra were recorded on discharged EDLCs at open circuit potential, by means of an Impedance/Gain-Phase Analyzer 1260 (Solartron Analytical) between 1 MHz and 10 mHz, with an AC amplitude of 5 mV. The data were analyzed by fitting the experimental spectra with the EQUIVCRT Boukamp software [17,18]. All simulations show good agreement with experimental results, as demonstrated by a $\chi^2 < 10^{-4}$. All electrochemical tests were performed in climatic chambers (KB115, Binder GmbH) with controlled temperature (20 °C ± 2 °C).

3. Results and discussion

Initially, the micro-morphology of the electrodes has been investigated via SEM. As displayed in Fig. 1a, no substantial differences can be appreciated between electrodes prepared with one or the other binder. Both polysaccharides allow the obtainment of homogenous coatings, where the carbon black particles are well distributed among the activated carbon particles. However, while

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