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Probing the characteristics of casein as green binder for non-aqueous electrochemical double layer capacitors' electrodes

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HIGHLIGHTS

- Casein is as water-soluble binder easily obtainable from waste food.
- Casein provides good mechanical, thermal and electrochemical stability.
- Optimized electrodes enable excellent performance in conventional non-aqueous electrolytes.

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ABSTRACT

Casein from bovine milk is evaluated in this work as binding agent for electrochemical double layer capacitors (EDLCs) electrodes. It is demonstrated that casein provides excellent adhesion strength to the current collector (1187 kPa compared to 51 kPa achieved with PVdF), thus leading to mechanically stable electrodes. At the same time, it offers high thermal stability (above 200 °C) and electrochemical stability in organic electrolytes. Apparently though, the casein-based electrodes offer lower electronic conductivity than those based on other state-of-the-art binders, which can limit the rate performance of the resulting EDLC. In the attempt of improving the electrochemical performance, it is found that the application of a pressing step can solve this issue, leading to excellent rate capability (up to 84% capacitance retention at 50 mA cm^{-2}) and cycling stability (96.8% after 10,000 cycles at 10 mA cm^{-2}) in both PC- and ACN-based electrolytes. Although the adhesive power casein is known since ancient times, this report presents the first proof of concept of its employment in electrochemical power sources.

1. Introduction

The role of the binder is often underrated in electrochemical energy storage devices. With the only function of keeping the electroactive materials together, it does not take an active role into charge storage processes and, therefore, it is considered as “inert” component. However, in spite of its role, the choice of the binder is crucial for the development of high performance as well as environmentally friendly devices. Actual electrode fabrication technologies involve the casting (or spraying) of slurries constituted by a mixture of the electroactive components dispersed in a binder solution/dispersion. Hence, the binder determines the solvent needed for the electrode production and, in turn, the overall process' sustainability. Polyvinylidene fluoride (PVdF) has represented for decades the state-of-the-art binder for Li-ion batteries electrodes [1]. With regards to electrochemical double layer capacitors (EDLC), both PVdF and Polytetrafluorethylene (PTFE) have been extensively used for organic- [2–4], aqueous- [5], as well as ionic liquid (IL)-based systems [6–8]. Nowadays, however, with the growing market of such devices, the employment of fluoropolymers is being questioned for several reasons. Besides containing fluorine, which makes them difficult to dispose at the end-of-life, PVdF, for example, requires the use of toxic solvents (i.e., *N*-methyl-2- pyrrolidone) that need to be properly handled to avoid health hazards, thus increasing the production costs. Water soluble

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binders provide, in these terms, considerable advantages.

In the past decade, a variety of natural and naturally-derived compounds have been proposed as binders for batteries [9–11], the most popular of which is Na-carboxymethyl cellulose (CMC) [12–20]. Nevertheless, just few works investigated the benefits of aqueous binders for EDLCs [3,21–24]. Yamagata et al. proved that alginate from brown seaweed enables better capacitance retention and lower cell resistance compared to PVdF and CMC, in both organic and IL electrolytes [24]. Aslan et al. also demonstrated the superior properties of polyvinylpyrrolidone (PVP, a synthetic but water soluble polymer) in both propylene carbonate (PC) and acetonitrile (ACN) electrolytes [3]. In our previous studies we proved that natural cellulose (NC) easily overperforms PVdF in terms of electrochemical stability at high voltages in IL [22]. Furthermore, we recently proposed potatoes starch as advanced water-soluble binder for EDLCs [23]. Given its amylopectin content, starch provides enhanced mechanical stability and suppresses phenomena such as cracking of the coating (typical of CMC), thus enabling higher mass loadings which result on larger areal capacitances.

Besides natural polysaccharides, protein-based compounds also provide excellent adhesive power. Extracted from skin and bones of animals (e.g., rabbit and fish glues), collagen has been indeed exploited for wood furnishings and mural paintings since ancient times. Although the use and production of natural adhesives has collapsed after the advent of synthetic resins, some protein-based adhesives are still in use nowadays. Among these, casein is probably the most common. Caseins are a class of proteins that can be extracted from mammalian milk and used for the fabrication of very strong adhesives [25]. Making use of eatable sources for producing binders might sound ethically unacceptable, however, our society wastes large amount of food every day. A recent study from Edinburgh University reports that, only in UK, 360,000 tonnes of milk is poured down the drains each year. Almost 50% of such waste is the result of too much being served, with the rest discarded for being sour or past its sell-by date [26]. Employing casein extracted from expired milk as binder in electrochemical devices would represent a cheap and sustainable way to dispose such food waste.

In this work we evaluate, for the first time, the possibility of using casein to fabricate electrodes for non-aqueous EDLC. Investigating all the important properties, from adhesion strength to electrochemical performance, we try to identify advantages and drawbacks of casein versus other natural binders, such as CMC, and state-of-the-art synthetic polymers, e.g., PVdF. The results of our study clearly show that casein can be employed in both propylene carbonate (PC)-and acetonitrile (ACN)- based EDLCs. The promising electrochemical performance and durability obtained after electrode optimization prove the potential of this old binder in this new application.

2. Experimental

2.1. Electrode preparation

EDLC composite electrodes were produced by aqueous processing of casein-containing slurries. The commercially available Na-salt of casein (from bovine milk, Sigma Aldrich) was firstly dissolved in ultrapure water (milliQ), by simple mechanical stirring at RT, to obtain a 5 wt% solution. After complete dissolution, conductive carbon (SuperC45 from Imerys Graphite and Carbon, hereinafter called CC) and activated carbon (DLC Super 30 from Norit, hereinafter called AC) were added to the colourless/yellowish solution. The addition of few drops of ethanol helped to suppress the formation of bubbles initially observed after the introduction of AC and CC in the slurry. After further stirring for 1 h, the black homogeneous ink was casted onto pre-etched Al foil using a blade coater with a wet coating thickness of 200 μm. The casted electrodes were left to dry in air for few hours before being transferred in an oven set at 80 °C and further dried overnight. For sake of comparison, composite electrodes employing Na-carboxymethyl cellulose (Walocel CRT GA07, Dow Wolff Cellulosics) and PVdF (Solef 6020, Solvay) were prepared by following the same above-mentioned procedure. Of course, in the case of PVdF water was replaced by *N*-methyl-pyrrolidone (NMP). Depending on the rheological properties of the binder, little amounts of solvent were added during the process to adjust the viscosity. The choice of PVdF was dictated by consistency reasons. PTFE is probably even more popular than PVdF in the EDLC field. However, as it does not allow direct casting on Al foil, a different electrode manufacturing method would be required, thus, hindering a direct and fair comparison with CMC and casein. All investigated electrodes were constituted by AC, CC and binder in the 85:5:10 weight ratio (if not stated differently throughout the text) with an AC loading in the range 2.7–3 mg cm^{-2} and dry coating thickness between 70 and 80 μm.

2.2. Physico-chemical characterization

The electrodes' morphology was investigated by Scanning Electrode Microscopy (SEM). Micrographs were acquired with a ZEISS LEO 1550VP Field Emission Scanning Electron Microscope (acceleration voltage: 5 kV) after Pt sputtering of the samples.

Thermal and porosimetric properties of the composite electrodes were investigated by thermogravimetric analysis (TGA) and N_2 adsorption porosimetry, respectively. For such tests the electrode coating was removed from the current collector foil in order to avoid artefacts arising from the presence of etched Al (especially in the N_2 adsorption experiments). TGA analyses were conducted with a Discovery Q5000 (TA instruments) with a heating rate of 5 °C min^{-1} under N_2 flow. Specific surface area and pore size distribution were determined by means of an N_2 adsorption porosimeter (Autosorb IQ, Quantachrome Instruments) and calculated according to the BET and DFT theories (assuming slit-shaped pores), respectively.

The adhesion strength tests were run on a Z2.5 Zwick/Roel machine. Briefly, an electrode of defined area (6.45 cm^2) was fixed between two plane parallel plates with the help of double-sided adhesive tape (3 M tape). After a start phase, in which the specimen is approached before contact is established, the compression phase takes place. Within the compression phase the compression stress rises until a defined pressure level (2000 N) is achieved and then kept constant during dwell time (120 s), in order to allow the adhesive to contact the electrode. Afterwards the pull-off phase (1000 mm min^{-1}) takes place and the maximum tensile force is detected. The adhesion strength is calculated from the maximum tensile force or pull-off force related to the sample area.

2.3. Electrochemical characterization

For the electrochemical characterization, the casted layers were punched into disks with 12 mm diameter. A further dried step of 12 h under vacuum at 120 °C was applied, in order to remove any solvent or moisture residue, before being transferred in an Argon-filled glove box (LabMaster, Mbraun GmbH) with H_2O and O_2 < 0.1 ppm. Experiments were conducted both in 2- and 3-electrode Swagelok type cells. Symmetrical EDLC were assembled using two identical electrodes as positive and negative electrode. Cathodic and anodic stability of the single electrodes was instead studied in 3-electrode configuration using an oversized counter electrode (with a ten times larger active material loading;