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Influence of the binder nature on the performance and cycle life of activated carbon electrodes in electrolytes containing Li-salt

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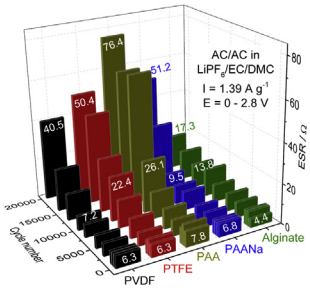
HIGHLIGHTS

- Alginate is a promising water-soluble binder for activated carbon.
- Optimized recipe provides stable slurries regarding the rheological properties.
- Activated carbon – alginate electrodes can last up to 20,000 cycles in $LiPF_6$/EC/DMC.

GRAPHICAL ABSTRACT



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ABSTRACT

In the current work, the influence of the binder nature on the mechanical and electrochemical stability of activated carbon (AC) electrodes in $LiPF_6$/EC/DMC is shown. Different binders employing water-based preparation route, i.e. poly(acrylic acid), sodium polyacrylate and sodium alginate, are evaluated and compared with the fluorinated binders (i.e. polytetrafluoroethylene, PTFE and polyvinylidene difluoride, PVDF). Results obtained during the investigation show that the rheological behavior of the slurry as well as the electrode porosity can be significantly affected by choice of binder. More precisely, slurries containing AC and alginate can experience the stress relaxation test without breaking down the polymer network due to the multiple bonds between AC surface and the carboxylic group of the pyranose ring of α-L-guluronic acid of the sodium alginate. Moreover, the AC-Alginate electrodes can sustain up to 20 000 cycles (~902 h) at I = 1.39 A g^{-1} in $LiPF_6$ without a great increase in total equivalent series resistance (ESR) ($ESR_{AC-Alginate,20000^{th}cycle} = 4 \times ESR_{1^{st}cycle}$, while $ESR_{AC-PVDF,20000^{th}cycle} = 6.5 \times ESR_{1^{st}cycle}$). The electrochemical impedance spectroscopy analysis on the aged electrodes shows that AC-Alginate can offer sufficient accessible porosity for extended charge/discharge cycles.

1. Introduction

Lithium-ion capacitors (LICs) have emerged to be a promising strategy to bridge the gap between lithium-ion batteries (LIBs) and electrochemical double layer capacitors (EDLCs) [1–3]. They exhibit higher energy density than conventional EDLCs and show not only better power capability than LIBs but also excellent cycling stability [3]. Depending on the electrode materials for LIBs used in LICs, EDLC materials can act as the positive or negative electrode in the device. In such hybrid systems, activated carbon (AC) is selected as the material of choice for supercapacitors due to its high surface area, tailored porosity, and low cost. If AC is chosen as the negative

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electrode and a lithium insertion material such as $LiMn_2O_4$ spinel or $LiCoO_2$ layered oxide as the positive electrode, the charge/discharge process is associated with the lithium ion transfer between the two electrodes [4–6]. However, if AC acts as the positive electrode and a lithium insertion material like $Li_4Ti_5O_{12}$ acts as the negative electrode, the anions in the electrolyte are adsorbed/desorbed on the surface of AC and simultaneously intercalation/de-intercalation process occurs between the lithium ions and the negative electrode during charge/discharge [1,3,7–13]. Hence, the electrochemical stability of AC as a positive or negative electrode in an electrolyte containing lithium salt play a major role in the electrochemical performance of the final device.

Conventionally, AC electrodes contains either poly(tetrafluoroethylene) PTFE or poly(vinylidene difluoride) PVDF as a binder. However, both binders suffer from their drawbacks such as limited cycle time or the use of toxic solvent like N-methyl-2-pyrrolidone (NMP) [14,15]. The development of safe, environmentally friendly electrodes is, therefore, essential for many electronic applications using lithium ion batteries and supercapacitors. This growing interest leads to the research of cheaper and greener electrode processing by using water soluble binders such as carboxymethyl cellulose (CMC), polyacrylic acid (PAA) or Alginate [16,17] (see Table 1). Most of these studies only focus on the processability of the new binder in Li-ion technology; less attention has been paid to its issue in EDLCs. It has been shown that green binders can also improve the cycle life of the EDLCs in the conventional electrolyte for supercapacitors such as $TEMABF_4$/PC or ionic liquid electrolyte [17–22]. For instance, Passerini's group prepared electrodes for EDLCs with natural cellulose as a binder and the resulting device showed high capacitance and excellent cycling stability [18,20]. Furthermore, they also observed superior performance with this binder under prolonged floating conditions at high cell voltages. Alternative to cellulose and their derivative, potatoes starch or casein as a green binder for non-aqueous EDLCs has been evaluated showing a significant enhancement of the adhesion between the coating layer and the current collector; extended cycle time was observed thereby [21,22]. Another member of the polysaccharide family – sodium alginate – derived from brown seaweed has also been proposed as a green binder for EDLCs [17]. EDLCs with this binder exhibited excellent high rate capability due to the high affinity of alginate for the activated carbon. Nevertheless, the processability, as well as the long-term cycling behavior of these new green binders in a conventional electrolyte containing lithium salt for LIBs (i.e. $LiPF_6$/EC/DMC), has not been illustrated yet.

In the present study, the influence of polyacrylic acid (PAA), sodium polyacrylate (PAANa), and sodium alginate (alginate) as binders used with AC has been investigated in term of processability and cycle life. Symmetrical EDLCs were assembled using two identical AC electrodes and lithium metal as a reference to evaluate the differences between the positive and negative electrodes. For the sake of comparison, PVDF- and PTFE-based electrodes have been prepared as well. Process parameters such as rheological behavior and electrode pre-treatment will be shown. Besides, electrochemical characterization tests will be discussed and compared with the conventional systems.

2. Experimental

2.1. Electrode preparation

Composite electrodes were prepared by mixing activated carbon (Haycarb PLC) as active material and SuperP (Imerys, earlier Timcal) as conductive additive with a binder solution by using a dissolver (Dispermat, Fig. S1) in the following way: (i) the binder was firstly dissolved in NMP (Sigma Aldrich) in the case of PVDF (Solvay) or in millipore water in the case of water-soluble binder; (ii) activated carbon and SuperP were then successively added to the binder solution; (iii) the mixtures were finally adjusted with additional solvent (NMP or H_2O) to a solid content between 24% and 33%. The total solid content of the slurries with individual binder was optimized based on the processability in the laboratory dissolver. Details about activated carbon properties used in this work can be taken from Ref. [24]. Three green binders - PAA (Sigma-Aldrich), PAANa and Alginate (Sigma-Aldrich), were tested and compared to the conventional PVDF binder. PAANa was prepared in the laboratory by neutralizing PAA with $NaOH \cdot H_2O$ (Sigma-Aldrich) at a pH = 7.25. 0.5 wt% of SBR (Styron Europe GmbH) was added to the PAANa binder solution to optimize the adhesion of the electrode. Finally, the pH of all slurries with aqueous binder was checked before coating on the current collector.

Detailed recipes can be taken from Table 2. The dissolver was equipped with a water bath to keep the slurry at the constant temperature of 23 °C. The final slurries were coated onto the pre-etched Al foil (MCT, Japan) using doctor blade technique with a wet thickness of 150 μm. The cast electrodes were dried at ambient temperature overnight (for aqueous binder) or first for 2 h at 60 °C and then at 80 °C overnight (for PVDF) to remove any residual solvent.

Since aqueous processing of AC electrodes was applied in the current investigation, coulometric Karl-Fischer titration (756/831 Karl-Fischer Coulometer, Metrohm) was carried out to determine the water content of the electrodes after a drying step at 130 °C under vacuum prior cells assembly. The titration cell is equipped with a generator electrode combined with the diaphragm. Hydranal® Coulomat AG-Oven (Fluka –Sigma Aldrich) was used as a reagent for the titration. The samples were heated up to 200 °C. The moisture released thereby is transferred to the titration cell and then calculated by the Karl-Fischer titration.

For the sake of comparison, composite electrodes employing PTFE (3 M) as a binder were also prepared via a plastic preparation route [24]. To ensure satisfactory electrical conductivity, all electrodes were compacted under optimized pressures with a

Table 1
Typical binders used for fabrication of electrodes in LIBs and EDLCs [16,23].

	PVDF	CMC	PAA	Alginate
Solvent	NMP		H_2O	
Environmental	Very toxic		Friendly	
Properties	Highly non-reactive and pure thermoplastic fluoropolymer	Weak polyacid Suspension properties depend on the value of substitution degree	High concentration of acid functionality Electrode laminates rigid and brittle, easily undergo delamination during roll-to-roll electrode	Copolymer of 1 → 4 linked β-D-mannuronic acid and α-L-gulunoric acid → higher affinity to Si electrode [16]
Current collector	No pH control necessary	Stability depends on the pH: Al-collector stable within 4 < pH < 8.5 [23]		