Energy 119 (2017) 435–441

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Cellulose and activated carbon based flexible electrical double-layer capacitor electrode: Preparation and characterization

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ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form
5 December 2016
Accepted 10 December 2016

Keywords:
Natural cellulose
Self-standing electrode
Electric double-layer capacitor
Binder
Activated carbon

ABSTRACT

Supercapacitors are efficient electric energy storage devices with a wide range of possible applications. In this study, a natural cellulose-activated carbon composite material that can be used as an electrode in a flexible supercapacitor is prepared using a phase inversion technique. The composite material preparation and testing methodology are described and the electrochemical characteristics of the composite material are analysed as a function of the activated carbon (AC) to natural cellulose (NC) mass ratio. Analysis of the influence of the AC/NC mass ratio on the electrochemical characteristics of the composite material demonstrated the importance of optimal mass ratio determination prior to manufacture. To prove an applicability of the NC binder, the electrochemical characteristics of the composite material prepared with a NC binder are compared with those of a composite material with a standard poly(-vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) binder. The experimental results confirm the applicability of using NC as a binder in the preparation of a composite material that can be used as a flexible self-standing supercapacitor electrode.

1. Introduction

Electrical double layer capacitors (EDLCs), which are also known as ultra- or supercapacitors, are a promising technology for electric energy storage in devices, where high power density and long cycle lifetime are required [1,2]. For example, EDLCs are widely applied in internal start-up systems of combustion engines, for acceleration of electric vehicles, in backup power supply for electric devices, for load levelling, and for storage of electricity generated from solar or wind energy. EDLCs can be considered as an ideal complement to batteries or fuel cells in the energy storage systems of the future [3–5]. In addition, EDLCs can be used in portable and wearable electronic devices, which require small, light, thin and flexible energy storage [6–8], and flexible EDLCs are being considered for utilization in electrochemical actuators [9], which are expected to have great importance in robotics and for biomedical applications [10,11]. Moreover, the flexible graphene based supercapacitor with ionic liquid is being considered with purpose to meet the requirements of future electrical vehicles by Tamilarasan et al. [12].

The vast majority of studies on EDLCs have focused on development of the carbonaceous material properties [13–17] and improvement in the electrolyte characteristics [18–21]. Little attention has been paid to the environmental impacts of the materials used, the production processes, and end-of-life disposal [22]. Commonly used fluorinated thermoplastic binders such as polytetrafluoroethylene (PTFE) and poly(vinylidene fluoride) (PVDF) can be considered as sources of possible environmental pollution during use and complicate EDLC disposal at the end of the useful life of the supercapacitor [23]. Consequently, increasing interest is being shown in the application of green fluorine-free binders. For example, polyvinylpyrrolidone was proposed as an alternative to PVDF and PTFE binders by Aslan et al. [24]. As a lightweight, abundant, environmentally benign, recyclable and economically viable material, cellulose and cellulose-derivatives such as fibres, nanofibers and nanocrystals have been extensively used as a structural material in the research and technical development of energy storage devices [25]. Sodium carboxymethyl cellulose was successfully applied as a binder in lithium-ion batteries by Buqa et al. [26], and it is considered as a promising binder material for EDLCs by Aslan et al. [24]. In other works considering cellulose use in supercapacitors, cellulosic templates were used for the preparation of supercapacitor current collectors in Ref. [27]. The production of cellulose nanocomposite fibres was studied in Refs. [28–31] and the natural cellulose dissolved in an ionic liquid

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http://dx.doi.org/10.1016/j.energy.2016.12.038
0360-5442/

was proposed as a binder for EDLCs in Refs. [22,32].

One of the most popular techniques for the manufacture of cellulosic electrochemical cells is blending of different forms of cellulose with the active material. This technique was widely used for the cellulosic electrode creation [22,24–26,28–31]. Approaches that involve blending various polymers with different nanoparticles to produce films and membranes have been widely researched, and the suitability of such films and membranes has been studied for a number of different applications [33–38]. The addition of nanoparticles has an influence on the mechanical properties and morphology of polymer film [33–38]. Moreover, the addition of nanoparticles can change final film performance [37,38]. Therefore, the nanoparticle/polymer mass ratio, which plays essential role in the composite film formation, has to be investigated in order to ensure that a product with the desired properties is produced. However, the issue of the influence of the AC/NC mass ratio on the characteristics of cellulose composite material has not been extensively studied, and little research on the topic has been reported in the scientific literature.

This work analyses the effect of the AC/NC mass ratio on electrochemical characteristics such as specific capacity, internal resistance and capacity retention of a composite material that can be used as a flexible self-standing electrode in an EDLC. Natural cellulose is used as a binder for the activated carbon in manufacture of the composite material under study. The production process and test setup are described in detail. Analysis of the influence of the AC/NC mass ratio on the electrochemical characteristics of the composite material shows the importance of determination of the optimal mass ratio prior to manufacture. In addition, to prove applicability of the NC binder it is compared with a commonly used poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) binder and its advantages and limitations are discussed.

2. Material and methods

2.1. Materials

Ionic liquid (IL), 1-ethyl-3-methylimidazolium acetate, was acquired from BASF Oy (Basionics^{TM} BC01, CAS: 143314-17-4, assay > 98%) and used as received in preparation of an electrode casting solution. Cellulose (degree of polymerization 780, α-cellulose content >93%) was purchased from Domsjö pulp mill from Sweden and was employed as the electrode binder. Activated carbon C4386 (Sigma-Aldrich) with BET surface area of 1100 $m^2 \cdot g^{-1}$ was chosen as an inorganic active filler for the electrode. Sulphuric acid from Merck (CAS: 7664-93-9, assay 95–97%) was used to prepare a 1 mol sulphuric acid aqueous electrolyte. Poly(vinylidene fluoride-co-hexafluoropropylene) was used as a standard electrode binder for the electrode preparation and N-Methyl-2-pyrrolidone (NMP) was used as a PVDF-HFP solvent. PVDF-HFP was chosen instead of PVDF because PVDF-HFP polymer chains precipitate during phase inversion casting, due to non-solvent interactions, and form a more flexible structure than PVDF [39]. In addition, PVDF-HFP is more hydrophobic than PVDF [39]. The PVDF-HFP and NMP were purchased from Sigma-Aldrich. Deionized water was used in the preparation of the electrolyte, in all electrode samples (as a coagulant) and in storage of the samples.

2.2. Electrode preparation

The self-standing electrode was prepared by the phase inversion method [40] using activated carbon as the active material and cellulose as the electrode binder. The preparation process is illustrated in Fig. 1.

An appropriate amount of the cellulose was ground and dissolved in the ionic liquid under vigorous stirring at 90 °C for 12 h to produce a 5 wt% casting solution. Precise amounts of AC particles (13.0, 16.7, 20, 23.1 or 25.9 wt%) were dispersed in the ionic liquid and the dispersion was placed under an ultrasound homogeniser (Bandelin UW 2200) for 10 min to prevent possible formation of carbon particle agglomerates. The hot cellulose solution was added to the activated carbon dispersion and the solution was mixed by ultrasound for 5 min to ensure a homogeneous particle distribution. After mixing, a uniformly black cellulose solution containing activated carbon particles was obtained. The hot solution was then immediately distributed on a glass plate with an adjustable casting

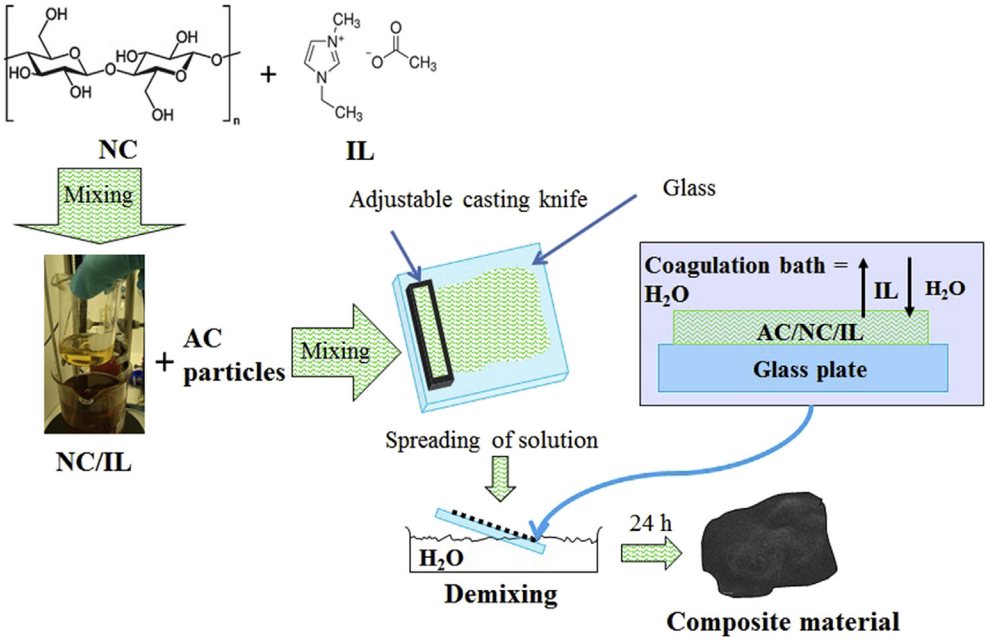

Fig. 1. Scheme of the cellulose composite material preparation.