Journal of Power Sources 391 (2018) 86–93

Contents lists available at ScienceDirect

Journal of Power Sources

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

Self-standing gel polymer electrolyte for improving supercapacitor thermal and electrochemical stability

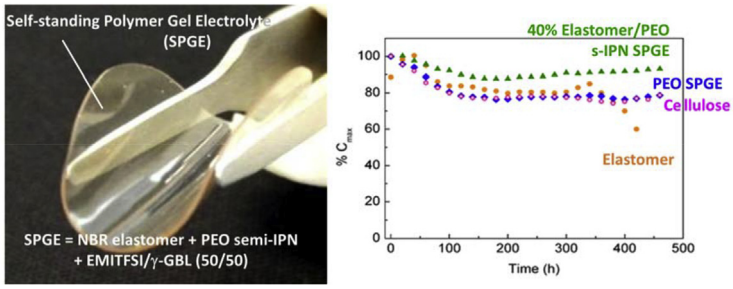
Laure Dagousset[a,b], Grégory Pognon[a], Giao T.M. Nguyen[b], Frédéric Vidal[b], Sébastien Jus[a], Pierre-Henri Aubert[b,*]

[a] Thales Research & Technology, 1 avenue Augustin Fresnel, 91767, Palaiseau, France
[b] Laboratoire de Physicochimie des Polymères et des Interfaces (EA 2528), Université de Cergy-Pontoise, 5 mail Gay-Lussac, 9503s1, Cergy-Pontoise Cedex, France

HIGHLIGHTS

- Solid Polymer Gel Electrolyte (SPGE) offering wide temperature range capabilities.
- SPGE synthesized directly in the presence of electrolyte.
- Large ESW: 3.2–3.6 V at 20 °C, up to 2.5 V at 100 °C only 1.8 V for cellulose separators.
- Good cycling and floating ageing of EDLCs.
- Exceptionally high stability of SPGE containing 40%NBR during floating at 100 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Supercapacitors
Solid polymer gel electrolytes SPGE
Widetemperature range
EMITFSI/gamma-butyrolactone
Floating at 100 °C
High stability

ABSTRACT

Electrochemical energy storage is a very active research topic. However, the use of liquid electrolyte in such systems as supercacitors presents several drawbacks on security and packaging. One way to overcome these issues is to design supercapacitors using solid-state electrolytes. We report here the one-pot synthesis and the characterization of self-standing gel polymer electrolyte (SGPE) composed of semi-Interpenetrating Polymer Networks (semi-IPN) based on poly(ethylene oxide) (PEO) network and non cross-linked nitrile butadiene rubber (NBR), self-containing EMITFSI/γ-Butyrolactone (50/50 wt%/wt%) binary mixtures. The SGPE under the form of a thin film are then used as solid electrolyte and also as separator in supercapacitors with Single Wall Carbon Nanotubes (SWCNTs) bucky paper as electrodes. Thermal characterization revealed the suitability of all synthesized membrane in wide range of operating temperature. Electrochemical stabilities of SGPE were close to that of a cellulose separator system (ESW ~ 3.2–3.6 V) at 20 °C, and were relatively higher than a cellulose system at 100 °C: 2.1–2.5 V and 1.8 V respectively. Furthermore, floating experiments at 100 °C (holding voltage at 2 V) revealed the exceptionally high stability of SGPE, with a residual capacitance of 93% after 500 h. This high electrochemical performance demonstrated the potential of semi-IPN SGPE as separator/electrolyte for high performance supercapacitors.

1. Introduction

Electrochemical energy storage is a very active research topic. Among studied systems, supercapacitors (SC) and more especially Electrochemical Double Layer capacitor (EDLCs) possess high power capabilities and can advantageously be used with batteries for strong

* Corresponding author.
E-mail address: pierre-henri.aubert@u-cergy.fr (P.-H. Aubert).

https://doi.org/10.1016/j.jpowsour.2018.04.073
Received 17 January 2018; Received in revised form 16 April 2018; Accepted 20 April 2018

energy peak demand during short times (devices power on, power interruption…). These EDLCs are generally constituted of two electrodes separated by a porous membrane impregnated with a liquid electrolyte [1–3]. Nevertheless, several drawbacks can be encountered such as electrolyte leakage, corrosion or packaging difficulties. The use of ionic liquids (ILs) instead of classical liquid electrolyte is very interesting given their important thermal stability as well as electrochemical stability window (ESW). However, despite their relatively high viscosity, ILs are in liquid state at room temperature, still presenting a risk of leakage. One way to overcome these issues is to design supercapacitors using solid-state electrolytes (SSEs). SSEs are ionic conducting materials commonly constituted of polymers. They can be used as electrolyte/separators with a dual function *i.e.* preventing electrical contact between the two electrodes to avoid short circuits and allowing good ion mobility between the two electrodes. One can distinguish two families of SSE: those without any solvent and those based on solid gel polymer. The first family consists of solid polymer electrolyte (SPE) where dissociated salt is dissolved in a polymer matrix, polyelectrolyte and polymeric ionic liquids (PIL) which are a subclass of polyelectrolytes having ionic species with chemical structure similar to the one of ionic liquids [4]. Nevertheless, in such systems, the conductivity barely reaches 10^{-5} S cm^{-1} at 25 °C, in the best case. Therefore, they are unfortunately unsuitable for use as electrolyte for high power applications such as supercapacitors [5–8].

Solid gel polymer electrolytes can be divided into three categories: hydrogel (containing water), organogel (containing organic solvent) and ionogel (containing ionic liquid) [9,10]. They are promising in energy applications by combining the advantage of solid state electrolyte and the high ionic conductivity of liquid electrolyte. SGPEs are prepared by incorporating a large quantity of liquid electrolyte to a polymer matrix forming a stable gel. They can be physical gel or crosslinking gel. Hydrogels generally use natural or synthetic polymers [9]. However, they are limited by their narrow ESW of *c.a.* 1.2 V. Organogel used generally poly(ethylene oxide) (PEO) [10] or poly(methylmethacrylate) (PMMA) as polymer matrix and usually display ESW of approximatively 2.0 V [11]. Nevertheless, their ionic conductivity is dependent to the solubility of inorganic salt in the solvent. Ionogels appeared to be a trade-off between ionic liquid et SSE systems, which may be constituted of PIL [12,13] or non-ionic polymer swollen in IL [14–21].

The integration of ionogel in supercapacitor is recent. Ionogel constituted of PIL have been reported by G.A. Tiruye et al. [12,13] on supercapacitors based carbon electrodes. The ionogels were composed of a binary blend of poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (pDADMATFSI) associated with different ionic liquids of pyrrolidinium or imidazolium family [13]. The ionic conductivity was higher for ionogel based on small anions (FSI^- and DCA^-), and wider electrochemical windows were found for gels based on electrochemically stable pyrrolidinium cation and sulfonylimide anions ($TFSI^-$ or FSI^-). The best performances in supercapacitor configuration were obtained with $Pyr_{14}FSI$ gel, with a specific capacitance, specific energy and specific power of 150 F g^{-1}, 36 Wh.kg^{-1} and 1170 W kg^{-1} respectively, at an operating voltage of 3.5 V [13].

Ionogel based on non-ionic polymer are constituted generally of poly(vinylene fluoride-co-hexafluoropropylene) (PVdF-HFP) [18–20], PMMA [21] or PEO derivatives [22]. Pandey et al. [23] have elaborated an ionogel based on the hydrophobic ionic liquid 1-ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate (EMIFAP) entrapped within PVdF-HFP. The gel material, stable from 5 °C to 90 °C, possesses an electrochemical window of ~4.4 V and a high ionic conductivity of $\sim 2.0 \times 10^{-3}$ S cm^{-1} at room temperature. The supercapacitor exhibits a good cycling performance with ~82% capacitance retention after 10,000 charge–discharge cycles at 1 mA/cm^2. Recently, ionogels have been also reported by the synthesis of PEO based polymer network in the presence of an ionic liquid [15,24,25]. Chaudoy et al. [25] have synthesized PEO based ionogel using 1-propyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide ($Pyr_{13}FSI$) and achieved high ionic conductivity $\sim 1.6 \times 10^{-3}$ S cm^{-1}. The confinement of $Pyr_{13}FSI$ in the polymer network allowed a high anodic stability of the gel (4.5 V *vs* Li). The supercapacitor's capacitance remained stable after 2000 charge–discharge cycles at 1 A/g. Beyond ionogel based on polymer networks, interpenetrating polymer networks (IPNs) combining Nitrile Butadiene Rubber (NBR) networks and PEO networks swollen with 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) have been reported. The presence of NBR allowed obtaining very flexible gels, with high ionic conductivity ($\sim 10^{-3}$ S cm^{-1}), high thermal stability (> 300 °C) and high dimensional stability [22]. These materials found advantageously their application in the field of electro-chemo-mechanical actuators [26] and electro-optical devices [27].

Recently, we reported binary mixtures of imidazolium and pyrrolidinium based ionic liquids and γ-Butyrolactone (GBL) as supercapacitor electrolytes allowing reaching high ionic conductivity for a wide range of temperature (from −50 to 100 °C) [28]. In addition, they exhibited excellent behavior using buckypaper electrodes composed of Single Wall Carbon Nanotubes (SWCNTs) in this range of temperature and under ageing conditions [29]. Among the IL/GBL mixtures studied, EMITFSI/GBL (50:50 wt%/wt%) based supercapacitors exhibited the best results with a 22% capacitance loss at 100 °C and only 6.6% at −50 °C after 500 h ageing experiments (floating).

Since IPN macromolecular architecture and EMITFSI/GBL mixture have already proved their efficiency in different systems, we decided to combine them in order to design efficient SGPE for supercapacitor applications. We report here the synthesis and characterization of self-standing gel polymer electrolyte (SGPE) composed of semi-Interpenetrating Polymer Networks (semi-IPNs) based on PEO networks and non cross-linked NBR and self-containing EMITFSI/GBL (50/50 wt%/wt%) binary mixtures. The SGPE will then be used as solid electrolyte and also as separator in supercapacitors with SWCNTs bucky paper as electrodes. The electrochemical characterizations of the resulting supercapacitors are detailed in term of scan rate effect, electrochemical windows, as well as thermal and electrochemical aging.

2. Experimental

2.1. Materials

1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide - EMITFSI was commercially available from Solvionic (electrochemical grade 99.9%, H_2O% < 30 ppm). γ-Butyrolactone (GBL, analytical grade > 99.5%, H_2O% < 200 ppm) was purchased from Merck. *N*-methylpyrrolidone (NMP, 98%) was purchased from Alfa-Aesar. Nitrile butadiene rubber with 44 wt% acrylonitrile content (NBR, *M*w = 230 000 g mol^{-1}, Perbunan 4456F) is kindly offered by Lanxess. Poly(ethylene glycol) dimethacrylate (PEGDM, M_n = 750 g mol^{-1}, Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGM, M_n = 475 g mol^{-1}, Aldrich), dicumyl peroxide (DCP, 98%), are purchased from Sigma Aldrich and dicyclohexyl peroxydicarbonate (DCPD) from Groupe Arnaud. All chemicals were used as received. The silver wire was polished with sandpaper and impurities on the platinum grid were burnt away using a Bunsen burner. Single wall carbon nanotubes were purchased from Bucky USA (cleaned Single Walled Carbon Nanotubes (SWCNTs) 90 wt% BU-203). Cellulose separators (cut to 16 mm diameter) are Whatman filter papers (Cat No 1450 055).

2.1.1. Synthesis of single networks

Polyethylene oxide (PEO) single networks synthesis were inspired by the protocol as described elsewhere by L. Goujon et al. [22] PEO precursors (PEGM/PEGDM at 75:25 wt ratio) and electrolyte (EMITFSI/GBL at 50:50 wt ratio) are magnetically stirred together in a flask under argon for 25 min at room temperature. The weight proportion of PEO precursor/electrolyte is fixed at 50:50. DCPD (3 wt% with respect to the