

Supercapacitive properties of activated carbon electrode in electrolyte solution with a lithium-modified silica nanosalt



Ha Won Jung^a, Louis Hamenu^a, Hae Soo Lee^a, Mohammed Latifatu^a, Kwang Man Kim^b, Jang Myoun Ko^{a,*}

^a Department of Chemical and Biological Engineering, Hanbat National University, Daejeon 305-719, Republic of Korea

^b Research Section of Power Control Devices, Electronics and Telecommunications Research Institute (ETRI), Daejeon 305-700, Republic of Korea

ARTICLE INFO

Article history:

Received 9 January 2015

Accepted 2 February 2015

Available online 2 February 2015

Keywords:

Lithium-silica nanosalt

Supercapacitive properties

Activated carbon

Cyclic voltammetry

ABSTRACT

In this work, lithium-modified silica nanosalt (Li2O2) is solution-synthesized and used as a gel-forming additive in 1.5 M tetraethylammonium tetrafluoroborate (TEABF₄)/acetonitrile (ACN) electrolyte solution for the supercapacitor with activated carbon electrode. The electrochemical properties of the supercapacitor adopting the Li2O2 (5 wt.%) are investigated using linear sweep voltammetry, cyclic voltammetry, and complex impedance spectroscopy. By the addition of the Li2O2, the electrochemical stability of the electrolyte is improved over 4.0 V (corresponding to the current density below 0.6 mA cm⁻²) and higher specific capacitances at the scan rates of 10–500 mV s⁻¹ are obtained. Thus, the Li2O2 can be considered as a promising electrolyte additive to enhance the supercapacitive properties of activated carbon electrode.

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1. Introduction

Organic (non-aqueous) and aqueous electrolytes are commercially used in electrochemical supercapacitors to achieve a wide potential window (high electrochemical stability) with lower resistances. The non-aqueous electrolytes typically have higher internal resistance than the aqueous electrolytes, which can reduce the power density of supercapacitors. Meanwhile, the aqueous electrolytes with wide potential window are still preferred to increase the energy density of supercapacitors. Moreover, the aqueous electrolytes are much desired due to their ability to withstand explosion [1] for high-temperature applications. However, there exist an electrolyte leakage as a major drawback of conventional supercapacitors using the aqueous electrolytes [2,3]. A solution to solve this problem is to use of gel electrolytes [4–6] or solid polymer electrolytes [4,7–9] instead of the aqueous liquid electrolytes. Alternatively, the use of electrolyte additives can be a way to overcome the electrolyte leakage. Even when adopting the non-aqueous electrolytes, the electric double-layer capacitors with activated carbon electrodes could not operate over the voltage of 2.7 V or 3 V due to the presence of active groups on carbon surfaces

that can degrade the electrolytes at higher voltages [10–12]. Surface functional groups of some electrolyte additives may enhance the specific capacitance by the contribution of their own pseudo-capacitances [13–15].

The addition of lithium-modified silica nanoparticles has been considered as an efficient way to enhance the electrochemical performance of energy-storage devices such as lithium-ion batteries [16–18]. The previous studies on the lithium-modified silica nanoparticles used hydrophilic fumed silica (A200, Aerosil[®], Evonik) to succeed in fast ion conduction [16] and high lithium cycling efficiency [17]. In contrast, the use of hydrophobic fumed silica (R202, Aerosil[®], Evonik) was also proved to yield a lithium-modified silica nanosalt [18] as a decent electrolyte additive of lithium-ion batteries by exhibiting superior electrochemical stability against the oxidation at higher voltages. In this study, the lithium-modified silica nanoparticle is solution-synthesized again to use as an electrolyte additive in 1.5 M tetraethylammonium tetrafluoroborate (TEABF₄)/acetonitrile (ACN) as a conventional electrolyte solution for activated carbon supercapacitors. The supercapacitor adopting the lithium-modified silica nanosalt additive (Li2O2) in the TEABF₄/ACN would be expected to exhibit the enhanced specific capacitance at higher scan rates, owing to the characteristic features of the lithium-modified nanosalt, such as higher electrochemical and interfacial stabilities.

* Corresponding author.

E-mail address: jmko@hanbat.ac.kr (J.M. Ko).

2. Experimental

Except for the kind of fumed silica used, the synthesis procedure of the lithium-modified silica nanosalt was similar to the way described by Sun et al. [17] who used silica nanoparticles with surface hydrophilicity. In this work, however, hydrophobic fumed silica (R202, Aerosil[®], Evonik; particle size 18–22 nm, surface area 100 m² g⁻¹) was used by preheating in a furnace at 300 °C for 3 days and transferring into a glove box filled with argon gas. At first, the R202 was added to tetrahydrofuran (99%, Duksan Chemicals) and stirred for 1 h to obtain a suspension. To the suspension, LiH (>99.9%, Aldrich) and 1 M lithium *tert*-butoxide (Li*t*BuO) (>99.9%, Aldrich) in tetrahydrofuran were added and stirred for 2 h at room temperature. Then, 1,3-propanesultone (99%, Aldrich) was added, stirred for 6 h at room temperature, and finally ultrasonicated for 30 min at 30 °C. The suspension was centrifuged and the solvent components were decanted. The residue was washed with excess tetrahydrofuran three times and dried at 100 °C for 3 days to obtain the lithium-modified silica nanosalt (Li202). The synthesis procedure and identification results in detail could refer to the previous report [18].

Two electrolyte solution samples of ‘Electrolyte’ (1.5 M TEABF₄ in ACN) and ‘Electrolyte’ + Li202 (5 wt.% added) were prepared to compare the electrochemical properties of electrolyte systems and the supercapacitive properties of activated carbon supercapacitor adopting the electrolyte systems. The TEABF₄ (99%) and anhydrous ACN (99.9%) were provided from Aldrich. Chemical structures of all the electrolyte components and the additive Li202 are shown in Fig. 1. Room-temperature ionic conductivities of the electrolyte samples were measured by complex impedance spectroscopy using an Autolab instrument (PGstat 100, Eco Chemie). To evaluate the electrochemical stability of the electrolyte samples, linear sweep voltammetry was performed at 10 mV s⁻¹ over than potential range of 0–5 V using a pouch-type cell consisting of platinum foils (1 mm × 1 mm) as working and reference electrodes.

The activated carbon electrode for supercapacitor was prepared from a viscous slurry composed of the activated carbon (MSC-30, Kansai Cokes) as an active material, poly(vinylidene fluoride) (Aldrich) as a polymeric binder, and vapor-grown carbon fiber (Showa Denko) as a conductive agent (8:1:1 weight basis, respectively) in *N*-methyl-2-pyrrolidone (Aldrich) as a solvent. Using a doctor blade apparatus with a gap of 250 μm, the slurry was coated on an aluminum foil (15 μm thick) as a current collector and dried at 120 °C to evaporate the solvent component and finally to yield the activated carbon electrode (70 μm thick including the aluminum foil). Prior to cell fabrication, the activated carbon electrode for supercapacitor was further dried overnight in a vacuum oven at 60 °C for 2 days. Cell assembly was done using a symmetric pouch-type cell in which the activated carbon electrodes

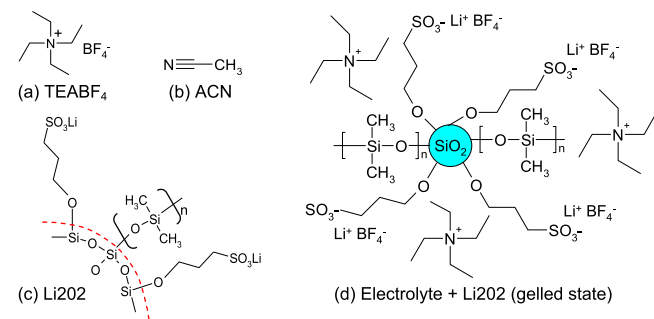


Fig. 1. Chemical structures of the electrolyte components and additives in this study. (a) TEABF₄, (b) ACN, (c) Li202, (d) Electrolyte + Li202 (gelled state).

(1 mm × 1 mm) were used to sandwich a SiC mat separator. Before sealing the pouch-type cell, the electrolyte solutions based on 1.5 M TEABF₄/ACN (‘Electrolyte’ and ‘Electrolyte’ + Li202 each) were injected. Cyclic voltammetry was conducted using an Autolab instrument (PGstat 100, Eco Chemie) in the potential ranges of 0–3.5 V and 0–3.8 V at various scan rates from 10 to 500 mV s⁻¹. The specific capacitance (*C*) was calculated as a function of scan rate using the equation $C = |q_a + q_c| / (2m\Delta V)$, where *q_a*, *q_c*, *m*, and ΔV denoted anodic and cathodic charges on each scan, mass of the active material, and potential window of the cyclic voltammetry. Complex impedance measurement was also performed for the supercapacitor cell using a frequency response analyzer instrument in the frequency range of 10⁻²–10⁵ Hz.

3. Results and discussion

Nanoceramic fillers have been used to achieve the enhanced electrochemical properties in many energy storage devices such as lithium-ion batteries [16–18] and supercapacitors [19]. With the addition of 5 wt.% of the Li202 into the conventional liquid electrolyte, significant improvements in ionic conductivity could be obtained over a wide temperature range [18]. The silica-based nanoceramic fillers may lead to form porous networks with the liquid electrolytes to yield a gel-state electrolyte [20] that can promote an easy conduction of ions to and from the electrode surfaces. In this study, though not arriving at an electrolyte with a perfect gel-state yet, slightly gelled surface between tiny flocculates are exhibited in the ‘Electrolyte’ + Li202 (5 wt.%) electrolyte sample (not shown in the figure). This may be due to the ionic liquid-like property of TEABF₄ associated with the Li202 nanosalt may encourage fast ion-conduction and performance stabilities (e.g., electrochemical and interfacial) by the brush-like structure of the ethyl (–CH₂CH₃) side group in the tetraethylammonium cation ((CH₂CH₃)₄N⁺) and the long-chain groups of polydimethylsiloxane (–[OSi(CH₃)₂]_n–) and propane lithium sulfonate (–(CH₂)₃SO₃Li) capped on the silica nanoparticles in the Li202.

That is, the conduction mechanism in the present electrolyte system of 1.5 M TEABF₄/ACN + Li202 (5 wt.%) may be considered in terms of three speculative concepts: (i) the association of BF₄⁻ with Li⁺ in the long chain of propane lithium sulfonate group, (ii) weak interactions between propane sulfonate anion and tetraethylammonium cation, which may be hindered by four ethyl side groups in the TEABF₄ salt, and (iii) the enhancements of electrochemical and interfacial stabilities by the polydimethylsiloxane groups [18,21] attached on the silica nanoparticles. As shown in

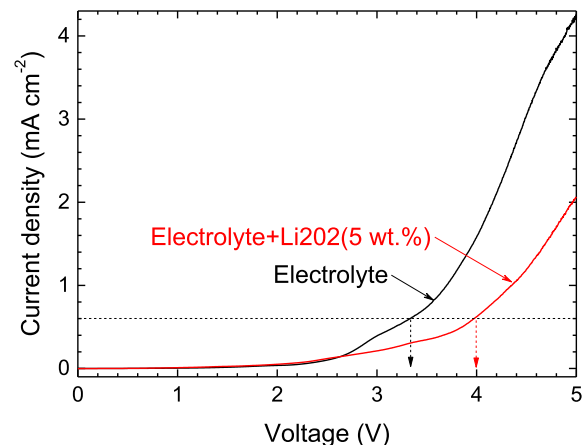


Fig. 2. Linear sweep voltammetry result obtained at the scan rate of 10 mV s⁻¹.

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