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High voltage electric double layer capacitor using a novel solid-state polymer electrolyte[☆]



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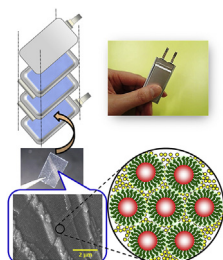
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HIGHLIGHTS

- We fabricated a leak free, EDLC cell with a 7.5 V operating voltage.
- The high voltage was achieved by a bipolar design and a new polymer electrolyte.
- The cell showed good cycle durability, low leakage current and self discharge.

GRAPHICAL ABSTRACT



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ABSTRACT

We designed and fabricated a bipolar-type electric double layer capacitor (EDLC) with a maximum 7.5 V operating voltage using a new concept in solid electrolytes. A cell having a high operating voltage, that is free from liquid leakage and is non-flammable is achieved by a bipolar design utilizing a solid polymer electrolyte made up of particles in a three-dimensional array, such as crystals composed of 75 wt% of hybrid particles decorated with a concentrated ionic liquid polymer brush (PSiP) and 25wt% of an ionic liquid (IL). The resulting solid film had sufficient physical strength and a high enough ionic conductivity to function as an electrolyte. Solidification as well as ionic conduction is due to the regular array of PSiPs, thereby producing a high ion-conductivity from a networked path between cores containing an appropriate amount of IL as a plasticizer. The demonstration cell shows a relatively good cycle durability and rate properties up to a 10C discharge process. It also has a very small leakage current in continuous charging and better self-discharge properties, even at 60 °C, compared with conventional cells. This paper demonstrates the first successful fabrication of a bipolar EDLC in a simple structure using this novel polymer solid electrolyte.

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[☆] Dedication: This research paper is dedicated to our late coworker Mr. Zenzo Hashimoto, President of CorePro R&D, Inc.

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1. Introduction

An electric double layer capacitor (EDLC) is an electrical energy storage device that physically stores electricity by forming an electric double layer consisting of adsorbed layers of cations and anions at the interfaces between the electrodes and the electrolyte.

Both the charge and discharge processes of this type of device are nonchemical reactions. Rather, they are Faradaic reactions, unlike a secondary battery and therefore it has a higher rate characteristic can be charged and discharged at a large current, and has a very long cycle life compared with rechargeable batteries [1–3]. Such devices are considered to be promising as a power source for mobile objects such as an automated guided vehicle, a hybrid electric vehicle and construction equipment. In these applications in particular, the high output performance of the EDLC are preferable for use in assisting the acceleration and smooth recovery of regenerative energy during deceleration.

Power density is an index of energy release and recovery of speed to/from the load. The maximum power (P_{max}) of EDLCs is represented by the following equations:

$$P_{max} = V_0^2 / 4R$$

Here, V_0 and R are the fully charged voltage of the EDLC and the internal resistance of the cell calculated from the voltage drop (IR drop) at the starting point of the discharge, respectively. The power density is defined either per weight (W/kg) or per volume (W/L) [4]. Increasing the cell voltage of an EDLC is a very important development goal, because the power density is proportional to the square of the cell voltage. Over the last ten years, researchers and developers have succeeded in improving the power and the energy density of EDLCs by using ionic liquids (ILs) as electrolyte solutes [5–7]. Generally, a salt having a melting point lower than 100 °C is defined as an ionic liquid. Ionic liquids are nonvolatile, have flame retardant properties and a relatively high ionic conductivity [8]. One manufacturer in Japan developed a high performance EDLC with a 3 V working voltage using an electrolyte that had a quaternary ammonium ionic liquid diluted with propylene carbonate. Some ionic liquids have a higher resistance to electrochemical degradation in the EDLC cell and a have a higher solubility in organic solvents used as an electrolyte than the solid ammonium salts conventionally used for EDLC electrolytes. Hence, using ILs, it is possible to make an electrolyte with high conductivity and durability against electrochemical degradation, resulting in a high power EDLC [3].

On the other hand, the most common cause of failure of electrochemical device products using liquid electrolytes is said to be liquid leaks. For the purposes of weight and cost reduction for the device, aluminum laminate film is used as the packaging material for many devices. However, because the solute in the electrolyte has surfactant properties, the electrolyte may continue to gradually penetrate the heat sealing portion of the package, and so it is very difficult to eliminate the possibility of leakage. With the aim of leakage prevention, much research on solid and gel electrolyte research has been performed to provide a large surface area with thin prismatic cell design and high processability [9–14]. As the electrochemical device involves movement of ions in the cell, a decrease in ionic mobility by solidification of electrolyte leads to spoiling of the power performance of the devices. Thus, a gel electrolyte with high ionic mobility is preferable and the fundamental concept of gel-polymer electro-chemical devices is to solidify the electrolyte by using the smallest possible amount of polymer material as a guest for the electrolyte [15]. There are some reports that an EDLC using a gel electrolyte can achieve higher capacity and power compared to a liquid system by making intimate contact between the active material on the electrode and the gel electrolyte [12–14].

Amid such developments, we have developed a totally new concept for the fabrication of a non-volatile, liquid leakage free and non-flammable solid electrolyte having a high ion-conductivity channel in a continuous network. This was constructed for the

first time by three-dimensional self-assembly in crystal like structure of hybrid silica particles (PSiPs) having “concentrated” polymer brushes (CPBs) of ionic-liquid type polymers on the silica surface and a small amount of ionic liquid (IL) that is included as a plasticizer. The regular array of CPB-modified particles was expected to provide a polymer-brush realm that was three-dimensionally continuously connected as a network array, in which the chain ends of graft polymers would be concentrated near the boundary region, leading to the expectation of enhancing the ion conduction in association with the segmental motion (Fig. 1) [16]. Since this polymer electrolyte, an ionic liquid type polymer-brush decorated silica particles/ionic liquids composite solid electrolyte (PSiP/IL solid electrolyte), also had good mechanical strength and a good ability to retain liquids, it became possible to produce a bipolar design that can provide a high voltage EDLC by a series connection between the electrode units in the cell package. Here we will present the design and the electrochemical performance of a high working voltage (7.5 V) EDLC cell using a PSiP/IL solid electrolyte.

2. Experimental

2.1. Materials

To prepare the EDLC electrolytes, the ionic liquid, *N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI) was purchased from Kanto Chemical Company Inc. and it was used after dehydration with molecular sieve (4A). The silica particles decorated with concentrated ionic liquid polymer brushes (PSiP) was prepared by the procedures described in our previous paper [16]. The preparation process is summarized in the schematic figure Fig. 1. We performed a surface-initiated atom transfer radical polymerization (ATRP) - a type of living radical polymerization (LRP) - by using *N,N*-diethyl-*N*-(2-methacryloyloethyl)-*N*-methylammonium bis(trifluoromethylsulfonyl)imide (DEMM-TFSI), a polymerizable ionic liquid as a monomer. This polymerization was started from the ATRP-initiating groups on the surface of monodisperse, 130 nm diameter, silica particles (SiP). This ATRP was well controlled, and gave a hybrid silica particle (PSiP) with an IL type of CPB with a relatively low polydispersity index and molecular weights up to about 100,000. The PSiP used for the solid electrolyte was obtained by polymerization at 70 °C for 14 h giving a polymer of $Mn = 25,000$ and polydispersity index (Mw/Mn) of 1.13 at a monomer conversion of 52%, where Mn and Mw are the number and weight-average molecular weight, respectively. The graft density per unit area was estimated to be 0.15 chains nm^{-2} . The surface occupancy (dimensionless graft density), σ^* was 0.33, indicating that 33% of the silica surface is occupied by the cross-sectional area of the fully stretched polymer brushes; for the calculation, the bulk density of poly(DEMM-TFSI) was assumed to be 1.4 $g\ cm^{-3}$. From the σ^* value, the ionic-polymer brush on the PSiP for the solid electrolyte was reasonably categorized as being in the CPB regime [16].

2.2. Preparation of electric double layer capacitor cell

The following procedure, illustrated in Fig. 2, was used for the fabrication of the high voltage EDLC cell. The carbon paint, comprising carbonized palm shell charcoal (surface area 2000 $m^2\ g^{-1}$, average pore diameter 20 nm, average particle size 8 μm), acetylene black and poly(vinylidene fluoride) [PVDF; average Mw ca. 534,000, purchased from Sigma-Aldrich Fine Chemicals Co. Ltd.] in *N*-methyl-2-pyrrolidone (NMP), was coated by a screen printing method using an HP-320 hand printer (Newlong Seimitsukogyo Co. Ltd.) with a thin metal mask (Bon Mark Co.

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