



A thin layer including a carbon material improves the rate capability of an electric double layer capacitor

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ABSTRACT

We present a new method to improve the rate capability of an electric double layer capacitor (EDLC) using a thin polymer layer having a high concentration of carbon material on a current collector (CLC). A novel thermocuring coating composed of a glycol-chitosan, a pyromellitic acid and a conductive carbon powder can form stable CLC on a metal foil current collector simply by spreading and curing at 160 °C for a couple of minutes. We compared the performance of some demonstration EDLC cells using three kinds of current collector: a conventional aluminum oxide foil for EDLC, an aluminum foil and an aluminum foil with CLC. The cell with the CLC had a much higher rate capability than the cell without CLC. Only the CLC cell was able to discharge at a current density of 500C. This cell shows a slight deterioration in capacity in a high temperature, continuous charging, life test, and the CLC has a suppressing effect on the internal resistance increase of EDLCs. The use of a CLC film current collector is one of the most effective and simple methods for the improvement of EDLC rate performance. In particular, a current collector consisting of aluminum foil coupled with a CLC promises to be a low cost alternative to the aluminum oxide foil commonly used in EDLCs.

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1. Introduction

An activated carbon-based electric double layer capacitor (EDLC) is an energy storage device based on the operating principle of the electric double layer that is formed at the interface between an activated carbon material and an electrolyte. This device stores electricity physically and lacks the chemical reactions found in rechargeable batteries during charging and discharging [1]. Therefore, compared to rechargeable batteries, the EDLC has a remarkably long cycle-life and high power density. Such devices are now widely used in power electronics for peak power saving and back up memories, and in electronic power supplies for automated guided vehicle systems and construction equipment. One of their most promising applications is for use in transportation, especially in hybrid electric vehicles (HEVs). However, in order to achieve the high power demanded by construction machinery and the smooth acceleration and the effective energy recovery needed during deceleration of vehicles, improvements in the charge and discharge rate property of the EDLC to provide a high power density are required.

In a previous paper [2], we focused on the role of the electrolyte, and reported that an EDLC including a quaternary aliphatic ammonium type ionic liquid diluted with propylene carbonate (PC) as an electrolyte has higher power and capacity characteristics at a low temperature compared with one using a conventional solid ammonium solute. Additionally, we showed that the ionic liquids containing the tetrafluoroborate anion had the best performance and stability for electric double layer capacitor applications [2,3].

On the other hand, in not only the EDLC but also in the lithium ion battery, the discharging capacity tends to deteriorate with an increase of the discharge current. To improve the rate capability of electrochemical devices, especially lithium ion batteries, various conducting agents having excellent electrical conductivity, such as carbon fibers (VGCs) [4], carbon nanofilaments (CNFs) [5], multi-walled carbon nanotubes (MWCNT) [6] and carbon nanobeads [7] have been investigated as electrode additives (especially for the anode). Also, in order to decrease the internal resistance of commercialized EDLC cells, that is, to improve their rate characteristics, conductive carbon materials, such as an acetylene black and Ketjen black, have been added to increase the passage of current between powdery activated carbon materials [2].

To further improve rate performance, we have prepared cells containing a carbon layer on the current collector (CLC). This consists of a thin layer having a high concentration of con-

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ductive carbon material, situated between the activated carbon electrode layer and the current collector. We have found that a hydroxyalkylated chitosan (glycol-chitosan) derivative and 1,2,4,5-benzene-tetracarboxylic acid (pyromellitic acid) mixture acts as a thermally activated binder that adheres strongly to metal foil was very effective in improving the rate capability of EDLC cells. Aluminum oxide foil has been generally used as a current collector in EDLCs although it is more expensive than aluminum foil. Because the internal resistance of an EDLC increases if an aluminum foil is used for the current collector, the rate capability that is the special feature of an EDLC is affected. However, surprisingly, an EDLC cell with CLC on the aluminum current collector shows an extremely high rate capability compared to a cell that has a conventional aluminum oxide collector. We believe that the CLC is one of the most promising developments that can achieve lower cost electrochemical devices while improving their rate performance. In this paper, we report the performance of a CLC-containing EDLC demonstration cell.

2. Experimental

2.1. Materials

To prepare the EDLC electrolytes, the ionic liquid *N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium tetrafluoroborate (DEME-BF₄) as solute was purchased from Kanto Chemical Company Inc., and it was dissolved in electrochemical device grade propylene carbonate (PC) purchased from Kishida Chemical Co. The 1 M DEME-BF₄ in PC solutions were then dried to less than 50 ppm (w/w) of moisture, as measured by a Karl Fischer titration in a dry atmosphere (dew point of air <−40 °C). To prepare a carbon thin layer on current collector (CLC), a mixed ink suspension, XSC-1N, produced by Kyoritsu Chemical & Co., Ltd. was used. The XSC-1N solution included acetylene black, glycol-chitosan, 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid) and *N*-methyl-2-pyrrolidone (NMP) as a solvent, in a weight ratio of acetylene black/glycol-chitosan/pyromellitic acid/NMP = 5/5/5/85.

2.2. Preparation of CLC

To form a CLC on a current collector, on an aluminum foil (thickness 20 μm) we spread a XSC-1N carbon ink suspension by use of a gravure printing method. The thickness of the printed layer was approximately 5 μm. After printing, the foil was dried at 160 °C in an oven to react chitosan and pyromellitic acid and evaporate the NMP solvent. The curing time was about 2 min. The current collector thus obtained, which contained 33% of acetylene black consisted of a 2.5 μm thick layer of CLC on the aluminum foil.

2.3. Fabrication of electric double layer capacitor cell

The electric double layer capacitors using 1.0 M DEME-BF₄ in PC as the electrolyte were prepared as previously described [2,8]. We used unpressed 20 mm × 40 mm square electrodes with a 100 μm thick activated layer for the demonstration EDLC cells. In this paper, to clarify the influence of the current collector on the EDLC performance, we constructed three kinds of cell using different types of current collector: an aluminum oxide foil (30 μm thick), an aluminum foil (20 μm thick) and an aluminum foil (20 μm thick) with CLC (2.5 μm thick).

2.4. Charge/discharge operation and other measurements

The assembled cell was charged in a constant current (CC) mode from $V = 0$ to 2.5 V at a constant current $I = 1.50$ mA. Under these conditions the current density was equivalent to 0.19 mA cm^{−2}. The

cell was then further charged to keep a constant voltage (2.5 V) for 15 min (i.e. CV mode). It was then discharged to 0 V at a given temperature T in a CC mode at a current varying from $I = 1.50$ to 750.0 mA. The corresponding energy output W was calculated from the discharge curve via the relation $W = \int IV dt$ [8]. The capacitance per unit weight was found by dividing the capacitance by the total weight of the active carbon material in a pair of electrodes. The thermal stability of an EDLC – a life test – was performed by continuous charging at 2.5 V and 60 °C. The cell deterioration was monitored by measuring its capacitance and internal resistance at 25 °C at given intervals. All data were the average value of three similar cells.

To carry out the EDLC testing, we used a HJ1010SM8 charge-discharging system, from HOKUTO DENKO Co. Ltd. Electrochemical impedance spectroscopic measurements were performed by an impedance analyzer (Princeton Applied Research VersaSTAT3-400 coupled with FRA) in the frequency range of 20 kHz to 10 mHz at 2.5 V full charged state. Scanning electron microscopy was performed on a JEOL JSM-6510.

3. Results and discussion

Chitosan is a natural and low cost biopolymer prepared by the deacetylation of chitin, the most abundant polymer after cellulose, and is mainly obtained from crab shells (Fig. 1). Due to its unique physicochemical properties such as non-toxicity, chemical and thermal stability, hydrophilicity, remarkable affinity towards certain substances and film formation with relatively high physical strength, it has been extensively studied and is used in many fields [9,10]. As an example of the application of chitosan in the field of electrochemistry, Fekry and Mohamed reported that a protective film of a chitosan derivative to be effective for corrosion control of a steel material [11], and Sugma and Cook also reported that poly(itaconic acid)-modified chitosan coatings mitigated the corrosion of aluminum substrates [12]. Some composite membranes of chitosan derivatives were also used as an electrolyte for a direct methanol fuel cell [13], and as a polymer electrolyte for a lithium ion battery [14,15]. We found that we could form a stable coating layer on the metal substrate by spreading and heating an ink composed of a glycol-chitosan and a polycarboxylic acid compound. Because it is well known that the secondary amino group of the chitosan forms an imide linkage by reacting with two carboxylic acids [10], we propose that such cross-linkage between chitosan molecules can be formed by use of a tetracarboxylic compound. It is probable that a stable three-dimensional polymer network had been formed by the synergistic effect of combining a chitosan with a relatively rigid backbone with a chemically stable imide cross-linkage (Fig. 1). In addition the amino group of the chitosan has a strong affinity to carboxylic and hydroxyl groups on the surfaces of inorganic materials [16]. Because the conductive carbon material used here, such as acetylene black and Ketjen black, has a lot of carboxylic acid and hydroxyl groups on the powder surface, it is likely that the chitosan binds strongly to them.

The chitosan dissolves easily in aqueous acids, though it does not dissolve in the NMP conventionally used as a solvent in electrode making. However, the chitosan can be converted into the amphiphatic partially hydroxyalkylated derivative obtained on reacting the hydroxyl and amino groups in the glucosamine unit with epoxide compounds such as ethylene oxide, propylene oxide and butylene oxide [10]. We developed a novel coating to use as a conductive layer on a metal current collector by reacting glycol-chitosan and pyromellitic acid [17].

In this study, we assumed that the cell impedance could be decreased by decreasing the contact resistance between the activated carbon electrode layer and the current collector. The method we employed simply places stable, thin carbon layer composed of acetylene black and glycol-chitosan (CLC) between the activated

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