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.

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 (VGCFs) [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-BF$_4$) 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-BF$_4$ 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 corrector (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-BF$_4$ 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 amphipathic 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
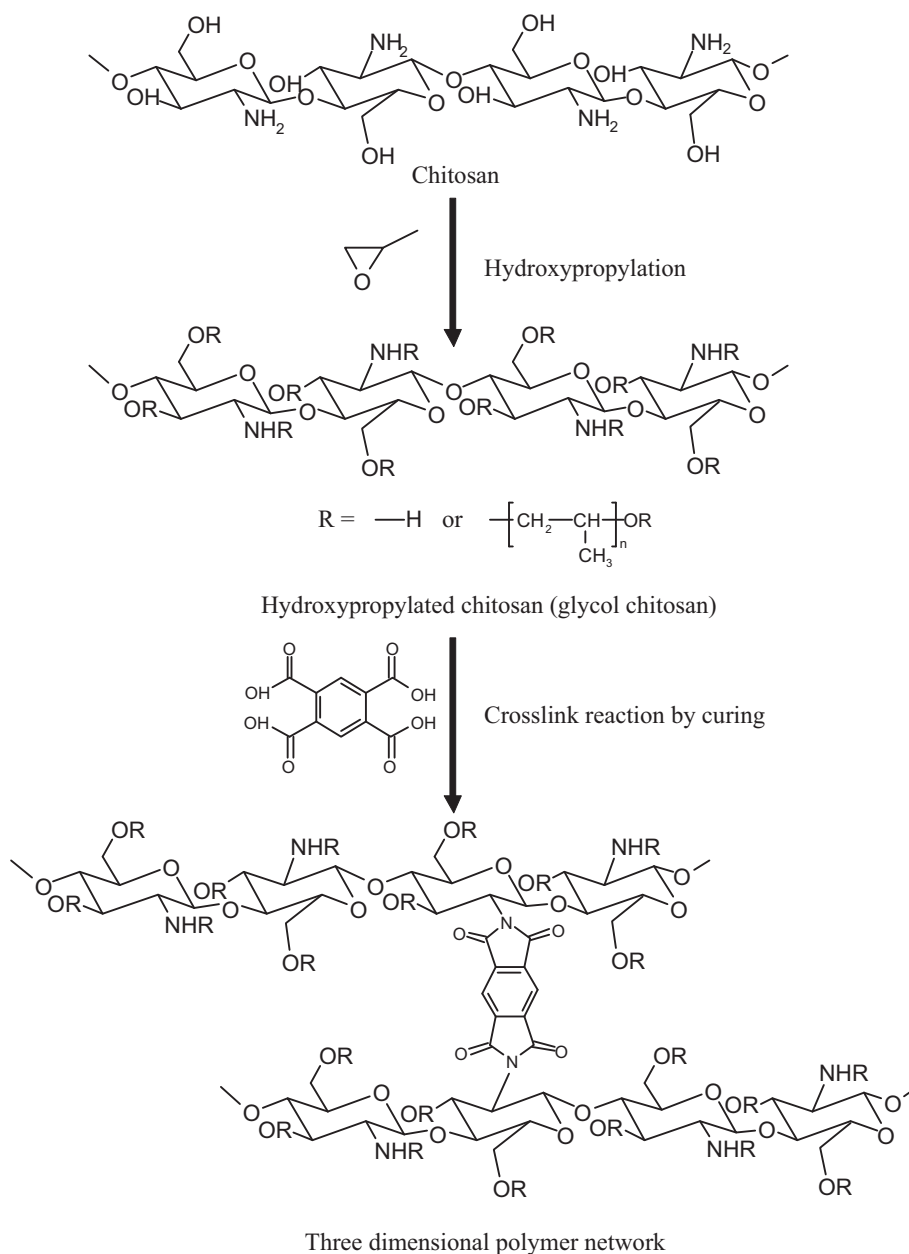
Fig. 1. Thermosetting chitosan/pyromellitic acid binder in this study.

carbon electrode and the current collector. The rate performance of demonstration EDLCs with, and without, a CLC on the current collector at 25 °C are summarized in Table 1.

The EDLC cell with an aluminum oxide current collector showed a slightly higher capacitance at low discharge current values. The pores present on the aluminum oxide foil surface might be con-

tributing to a small capacity increase. The conventional aluminum foil cell has the lowest capacitance of the examined cells, resulting from the large internal resistance of the cell, even for low rate discharging, such as that at 1C. On the other hand, the cell with a thin carbon layer on both positive and negative conventional aluminum foil collectors (CLC) showed an excellent discharge rate character

Table 1
Double layer capacitance of EDLCs with various current collectors at different discharging rate.

Current collector[a]		Discharge capacity C (Fg^{-1}) in various discharging rates[b]					
Positive electrode	Negative electrode	1C	20C	50C	100C	300C	500C
Al + CLC	Al + CLC	22.5	20.8	19.1	17.6	12.3	9.1
Al	Al + CLC	22.6	18.5	14.5	9.6	1.6	0.2
Al + CLC	Al	23.0	17.0	10.6	7.0	1.5	0.3
AlOx	AlOx	25.2	21.3	16.9	11.6	2.4	0.3
Al	Al	21.3	14.3	7.9	3.4	0.1	0.2

[a] Al + CLC, aluminum foil (20 μm) with 2.5 μm of CLC; Al, aluminum foil; AlOx, aluminum oxide foil (30 μm).
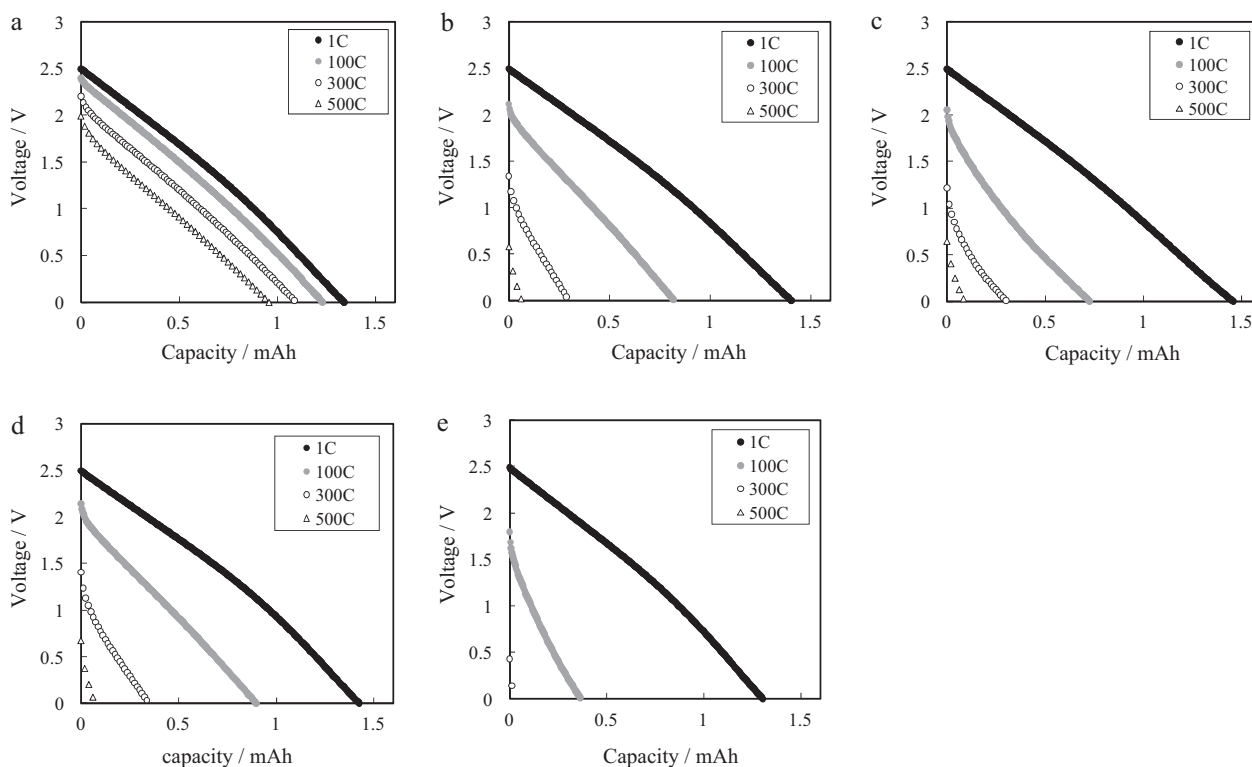[b] Constant discharging current of 1.5 mA corresponds to 1C and 0.19 mA cm^{-2}.

Fig. 2. Discharge curves of demonstration EDLCs using various current collectors at various current densities at 25 °C. (a) EDLC cell using aluminum foil with CLC on both electrodes; (b) cell using aluminum with CLC only on the negative electrode; (c) cell using aluminum with CLC only on the positive electrode; (d) cell with aluminum oxide foil on both electrodes; (e) cell with aluminum foil on both electrodes. The discharging rate of 1*C* corresponds to 0.15 mA of discharge current.

for an EDLC. Evidently, this cell has about the same capacitance as a common EDLC cell at 20*C* discharging, and at 50*C*, the discharging capacity of the CLC cell surpassed that of the common cell. The capacitance of the CLC cell at 300*C* discharging was five times larger than that of the common cell, and was thirty times for a 500*C* discharging process. At 500*C* discharging, corresponding to approximately 94 mA cm^{-2} of current density to the electrode surface area, the EDLC with an aluminum oxide could not discharge. However, the CLC cell maintained 40% of the capacitance at 1*C* discharging. These results indicate that the installation of a CLC had an extremely positive effect on the rate performance of the cell.

Fig. 2 shows discharging profiles of demonstration EDLCs at various discharge rates. Although the cell with a CLC on the negative electrode performed a little better in terms of rate one with a CLC on the positive electrode, both cells failed to exceed the rate performance of the aluminum oxide cell at all discharge rates. Because the resistance of an electrode without a CLC is rate-limiting, it is likely that the internal resistance of the cell increased and rate capability was spoiled as a result. The overall conclusion is that a CLC was necessary for both electrodes in order to improve the rate performance of EDLCs.

Nyquist plots for a demonstration cell in the frequency range from 10 mHz to 20 kHz are shown in Fig. 3. They consist of a semicircle at high frequency followed by an inclined line and a vertical line in the low frequency region. The intercept with the real axis at high frequency gives an estimate of the solution resistance (R_s). The diameter of semi-circle, namely the difference between the high frequency intercept (R_s) and low frequency intercept, indicates the
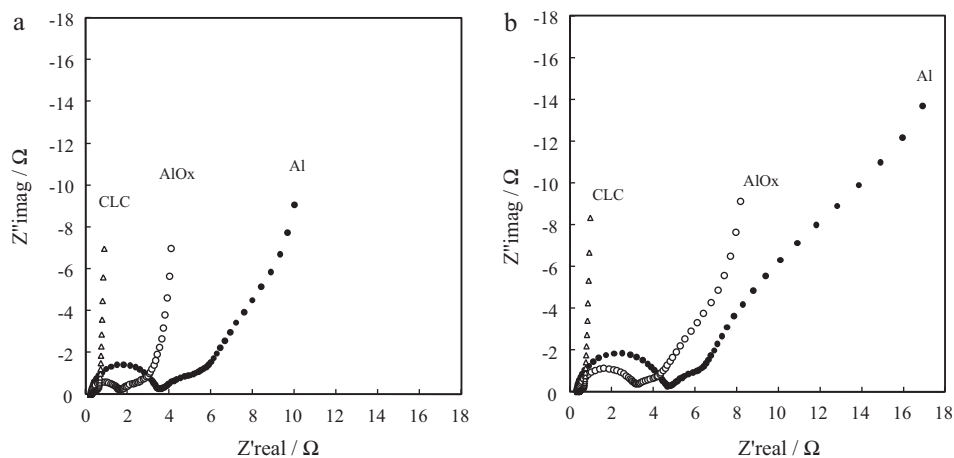

Fig. 3. Experimental Nyquist plots of demonstration EDLCs using various current collectors at 25 °C. (a) Fresh cell; (b) cell after life test, continuous charging at 2.5 V, 60 °C for 500 h. (CLC) = cell with aluminum foil with CLC on both electrodes; (AlOx) = cell with aluminum oxide foil on both electrodes; (Al) = cell with aluminum foil on both electrodes.
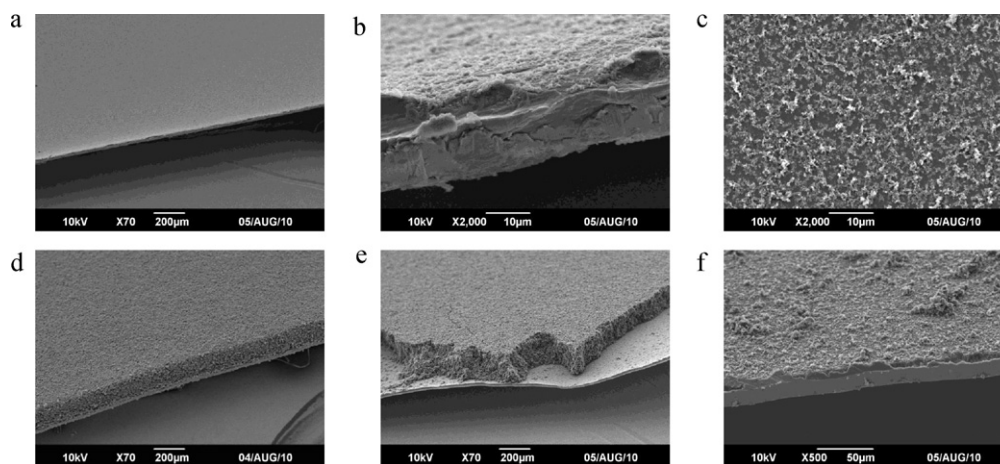
Fig. 4. Scanning electron microscopy images of aluminum foils with CLC and EDLC electrodes. (a)–(c) Aluminum foil with CLC; (d) EDLC electrode on aluminum foil with CLC; (e) EDLC electrode from which activated carbon layer is partially peeled off by cooling and bending in liquid nitrogen; (f) the surface of aluminum foil with CLC from which activated carbon layer has been partially peeled off by cooling and bending in liquid nitrogen.

interfacial resistance (R_i), which is attributed to the impedance at the interface between the current collector and carbon particles, as well as that between the carbon particles themselves [18,19]. The R_s value of each test cell was almost same. However, the diameters of the semicircles were different in each cell. The cell with CLC on both electrodes has a very small semicircle compared with other cells. The cell with the largest semi-circle was that with a conventional aluminum current collector. The activated carbon layer was prepared by the same methods and materials in each case, so the diameter of a semi-circle indicates the difference in the interfacial resistance between the activated carbon layer and current collector. The installation of a CLC has the effect of decreasing the interfacial resistance between the electrode layer including the active material and the collector. It is thought that the same effect can be expected even in the lithium-ion battery.

Fig. 4 presents SEM micrographs of aluminum foils with CLC and EDLC electrodes. In the low magnification image, although the CLC seems to be coated uniformly and smoothly in Fig. 4(a), the 2000× magnification image (c) reveals that the acetylene black particles are connected in a fibrous aggregate and spread over a wide area on aluminum surface like a reticulation, while Fig. 4(b) shows that the thickness of the fibrous aggregate is approximately 2–3 μm. To prepare the active carbon electrode layer we spread the ink mixture composed of activated carbon, acetylene black, poly(vinylidene fluoride) binder and NMP as a solvent on CLC. During this process, it is likely that the activated carbon particles enter the gaps in the reticulations, and the CLC integrates with the activated carbon as the NMP evaporates to form an electrically conducting path.

We tried to detach the activated carbon layer from the current collector of EDLC electrode (Fig. 4(d)) by cooling and bending it in the liquid nitrogen (Fig. 4(e)). In this experiment, the activated carbon layer peeled off from the electrode, leaving a thin layer behind. In Fig. 4(e) we did not observe detachment at the CLC and activated carbon interface, or at that between the CLC and aluminum foil. It was not possible to observe the CLC layer after it was peeled off, but a thin activated carbon layer can be seen remaining on the electrode in Fig. 4(f). These results confirm that the CLC bonds strongly bonds to the aluminum collector and the carbon electrode layer, and has the effect of decreasing the interfacial impedance.

In contrast to batteries, the cycling test is less important for an EDLC, because deterioration mostly occurs at the maximum operating voltage. So, as a more useful life test we continuously operated the cell at 2.5 V, 60 °C. Presumably, a good response to this test will indicate good durability at room temperature. The maintenance of capacity of demonstration cells after 500 h operation is summarized in Fig. 5. All cells showed a good practical level of durability, the capacity loss being just 8%, regardless of the presence of CLC. However, the interfacial impedance R_i of cells with conventional aluminum and aluminum oxide collectors increased after continuous charging at 60 °C, as shown in Fig. 3(b). In contrast, an increase in R_i was not observed for the cell with a CLC. We can conclude that a thermoreactive type of chitosan/pyromellitic acid binder has relatively high heat tolerance and electrochemical stability, and might act to suppress the generation of a high resistance material on the surface of the collector.

We opened the demonstration cell after the continuous charging examination and investigated the bonding between the electrode and current collector by rubbing the electrode surface with paper. The activated carbon layer of both electrodes with both the aluminum collector and aluminum oxide collector were peeled off easily by rubbing one or two times. However, that on the CLC was not separated even after rubbing more than 20 times. Both the interfacial bonding between the CLC and aluminum foil, and between the CLC and the carbon electrode remained completely intact. We can conclude that the CLC acted as a long-lasting internal adhesive layer that improves durability.
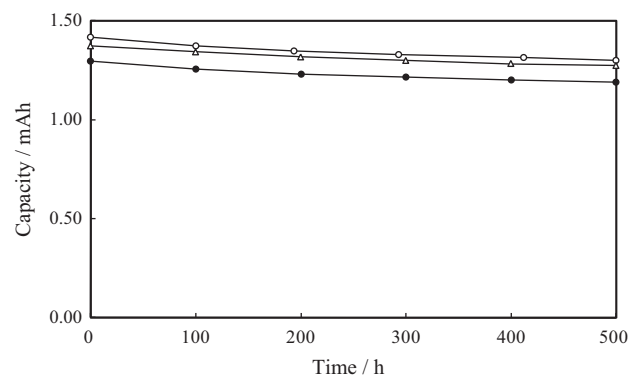

Fig. 5. Life test of demonstration EDLCs using various current collectors. The cell was continuously charged at 2.5 V, 60 °C for 500 h. The current collector used are: (open circle) aluminum oxide foil; (open triangle) aluminum foil with CLC; (filled circle) aluminum foil.

4. Conclusion

We have developed a new method that improves the rate capability of EDLCs. It comprises a very simple method of creating a thin polymer film containing a high concentration of carbon material (CLC) on the current collector that makes high power discharging at 500C possible. The novel thermocuring type of polymer binder made from a glycol-chitosan and pyromellitic acid mixture was extremely suitable for the CLC formation. It was revealed from impedance analysis that a CLC that was only 2.5 μm thick was effective in decreasing the interfacial impedance between the current collector and the electrode layer. The current collector made from a CLC on conventional aluminum foil showed a much better rate discharging property than the aluminum oxide current collector used in commercialized EDLC cells. A demonstration CLC cell could be discharged at the current density corresponding to rate of 500C, while the aluminum oxide cell could not be discharged at that rate. The CLC cell showed a high durability in a continuous charging test at 60 °C for 500 h, and had the effect of suppressing an increase in the interfacial impedance between the current collector and the activated carbon electrode. The use of a CLC film on a current collector is one of the most effective and simple methods for the improvement of EDLC rate performance. Because this CLC technology can be applied to various electrochemical devices, in the near future we will report on the application of a CLC to the lithium ion battery.

Acknowledgements

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