All-Solid State Electric Double Layer Capacitor Using Polymer Electrolyte and Isotropic High Density Graphite Electrodes

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Isotropic high density graphite (HDG) was used as the polarizable electrode of electric double layer capacitors (EDLC) with a solid electrolyte consisting of $PEO/LiClO_4([EO]/[Li^+]$ = 8:1) at 80 ℃ or with a gel electrolyte consisting of PEO/PC/$LiClO_4$ ($[EO]/[PC]/[Li^+]$ = 8:8:1) at room temperature. The all-solid state capacitor with HDG electrodes works satisfactorily as a EDLC with a relatively high capacitance, as well as the EDLC with gel electrolyte PEO/PC/$LiClO_4$. These EDLCs with solid polymer electrolyte PEO/$LiClO_4$ and gel electrolyte PEO/PC/$LiClO_4$ show good charge/discharge behavior when charged to 1.5 V at 80 ℃ and 20 ℃, respectively.

Recently a power-capacitor is envisaged, for example, as a useful complement to batteries in the electric vehicle.[1,2] Solid polymer electrolytes have been used in lithium batteries,[3,4] because they can lead to high reliability without leakage of the electrolyte; especially, they can provide a high energy density when used as an ultrathin film solid electrolyte. The application of solid polymer electrolyte to the construction of electric double layer capacitor (EDLC) is also attractive. However, there are only a few attempts made for such applications for the following reasons: the relatively low conductivity of most polymer electrolytes at room temperature, the poor electrical contact at the electrode/electrolyte interface, and the adverse effect of crystallized domains of polymer electrolyte without ionic conductivity. Ishikawa et al.[5] successfully employed the gel electrolyte using ACF at room temperature. The PEO/$LiClO_4$ electrolyte has been widely discussed as a solid polymer electrolyte for all-solid state secondary lithium batteries,[3] but it apparently has not been used for the preparation of EDLC.[5] In this letter, we report the results of our study on the possibility of constructing an all-solid state capacitor using carbon electrodes and PEO/$LiClO_4$ as a solid polymer electrolyte. We found that isotropic high density graphite (HDG) is one of the candidates for the polarizable electrode of EDLC in regard to the magnitude of differential capacity and the charge-discharge performances .

A phenolic resin-based activated carbon fiber cloth (ACF, specific surface area: 2000 m^2 g^{-1}, Kuraray Chemical Ltd.) and flat electrodes were used. The flat electrodes were an HDG plate (specific surface area: 0.809 m^2 g^{-1}, pore diameter: 0.42 μm, bulk specific gravity: 1.90 g cm^{-3}, Toyo Tanso Ltd.), a copper foil coated with a 60 μm thick conducting carbon paint ("Eburiom", Nippon Kokuen Ltd.), a copper foil coated with a vapor deposited carbon film (ca. 100 Å thick), and a copper foil (70 μm thick) without any coating material, respectively. The apparent surface area of all flat electrodes was 1.13 cm^2. For the polymer electrolyte, a 100 μm thick PEO/$LiClO_4$ ($[EO]/[Li^+]$=8:1) solid electrolyte was employed, For comparison, a PEO/PC/$LiClO_4$ ($[EO]/[PC]/[Li^+]$=8:8:1) gel electrolyte film with the same film thickness and supporting salt concentration was used. The PC ratio is the maximum content for $[EO]/[Li^+]$=8:1, because the continuous solid film could not be obtained with greater PC contents. The electrolyte films were prepared by casting on Teflon plates and dried at room temperature for over 48 hours. The EDLC was then constructed with a pair of the above electrodes as a model capacitor. Electrochemical measurements were performed using a sandwich type cell at 80 ℃ for the solid polymer electrolyte

Table 1. Electrode material dependence of capacitance of EDLC using PEO/$LiClO_4$ ($[EO]/[Li^+]$=8:1) solid polymer electrolyte at 80 ℃

Electrode	a	b	c	d
Capacitance (μF cm^{-2})	0.8	29.6	8	770

a: copper foil, b: Eburiom of conducting carbon paint film, c: vapor deposited carbon film, d: HDG plate.

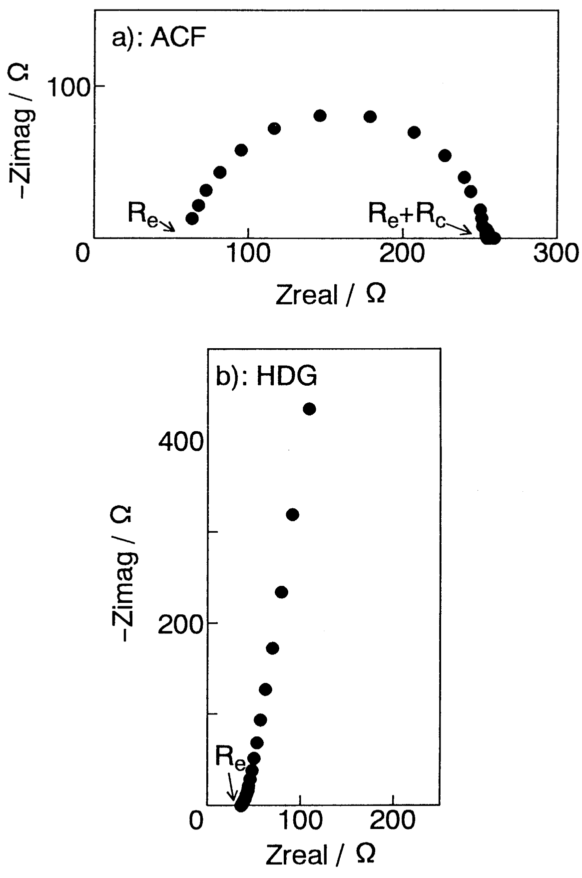

Figure 1. AC impedance responses of capacitors using PEO_8-$LiClO_4$ solid polymer electrolyte at 80 ℃. a). ACF electrode, b). HDG electrode.

Table 2. Comparison of characteristics for solid electrolyte and gel electrolyte EDLC using HDG electrodes(1.13 cm^2)

Electrolyte	Temperature (℃)	Cutting voltage	Capacitance (mF)	Internal resistance (Ω)	Leakage current (μA)	Coulombic efficiency (%)
PEO_8-$LiClO_4$	80	1.5 V	0.61	23	7.7	87
PEO_8-$LiClO_4$	20	1.5 V	—	1600	—	—
PEO_8-PC_8-$LiClO_4$	20	1.5 V	0.52	169	4.2	95

and at 20 ℃ for the gel electrolyte. Cyclic voltammetry of the cell was performed from -0.8 V to 0.8 V applied between the two electrodes at 10 mV s^{-1}. The ac impedance spectroscopy was carried out at open circuit voltage from 20 kHz to 10 mHz. The capacitor was charged to 1.5 V, then discharged to 0 V at 0.1 mA of constant cycling current.

The ACF electrode is known to exhibit a high capacity in aqueous or organic media. Thus, we tried to apply it to the solid polymer electrolyte system, but the all-solid capacitor prepared with ACF did not function as a capacitor. The ac impedance response of the cell with ACF electrodes is shown as the semicircle in Fig. 1(a), which corresponds to the electrolyte resistance R_e and the higher contacting resistance R_c . In fact, this solid electrolyte hardly fills up micropores of the ACF, and thus the results become semicircular. On the other hand, the ac impedance response of the capacitor using plate electrodes usually yields a nearly vertical straight line as shown in Fig. 1(b), which shows ac impedance response of an EDLC using HDG plate electrodes, exhibiting a typical response of capacitors. Furthermore, with this type of capacitors, a high capacity can be obtained by stacking thin capacitor units without using current collectors. With ACF electrodes this mode of capacitor construction is difficult to apply. We calculated the capacitance of various flat electrodes from the ac impedance response, and the values are given in Table 1. It was found that the HDG electrode yielded the largest capacitance among the various flat electrodes. This might be due to the surface morphology in the HDG electrode. Cyclic voltammograms for these HDG electrode EDLCs in solid electrolyte PEO_8-$LiClO_4$ at 80 ℃ and gel electrolyte PEO_8-PC_8-$LiClO_4$ at 20 ℃ are shown in Fig. 2. Clearly, these results exhibit a good capacitor performance, suggesting

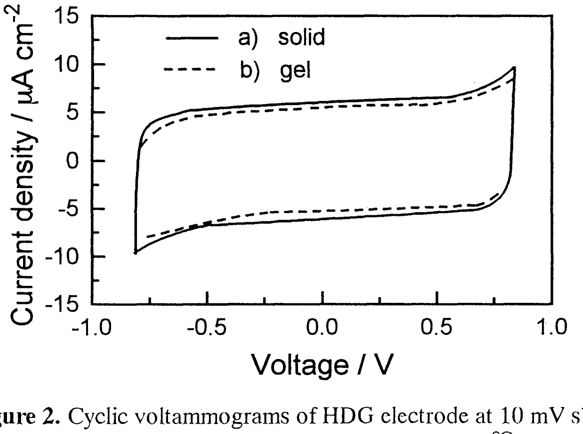

Figure 2. Cyclic voltammograms of HDG electrode at 10 mV s^{-1} in a) PEO_8-$LiClO_4$ solid polymer electrolyte at 80 ℃ and b) PEO_8-PC_8-$LiClO_4$ gel electrolyte at 20 ℃.

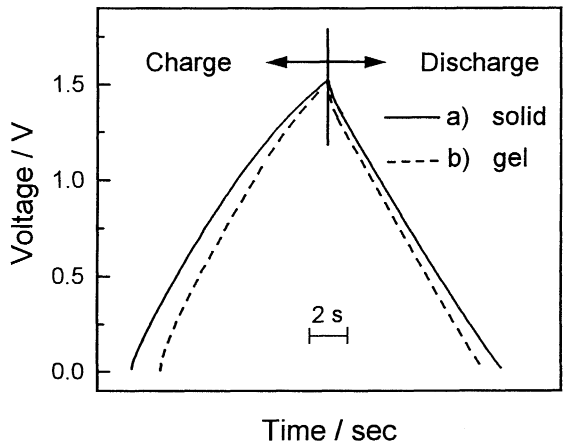

Figure 3. Charging-discharging curves at 0.1 mA cm^{-2} for EDLCs using HDG electrodes with a) PEO_8-$LiClO_4$ solid polymer electrolyte at 80 ℃ and b) PEO_8-PC_8-$LiClO_4$ gel electrolyte at 20 ℃.

that the HDG material is suitable for use in solid or gel polymer electrolyte for EDLC with a high capacity.

Figure 3 presents charge-discharge curves of an HDG/ PEO_8-$LiClO_4$/HDG capacitor at 80 ℃ and HDG/PEO_8-PC_8-$LiClO_4$/ HDG capacitor at 20 ℃ when charged to 1.5 V at 0.1 mA. The comparison of the above two capacitors is summarized in Table 2. As shown in Table 2, the EDLC performance was almost the same for the PEO_8-$LiClO_4$ solid electrolyte at 80 ℃ and for the PEO_8-PC_8-$LiClO_4$ gel electrolyte at 20 ℃. The PEO_8-$LiClO_4$ solid electrolyte at 20 ℃ yielded poor capacitor performance due to high internal resistance.

In summary, we have shown two principal results; one is that the HDG material gives a higher differential capacity than other flat electrodes, and the other is that the HDG electrodes for EDLC work well in PEO_8-$LiClO_4$ solid electrolyte at 80 ℃ and PEO_8-PC_8-$LiClO_4$ gel electrolyte at 20 ℃.

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