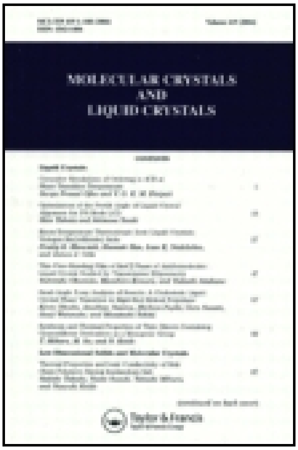

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Batteries and Electric Double Layer Capacitors Composed of Activated Carbon Fiber Electrode

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BATTERIES AND ELECTRIC DOUBLE LAYER CAPACITORS COMPOSED OF ACTIVATED CARBON FIBER ELECTRODE

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Abstract Commercially available activated carbon fiber (ACF) was used as a cathode of Li-battery and as electrodes of electric double layer capacitor. Charge-discharge characteristics and self-discharges of the cells were studied.

INTRODUCTION

New type of organic batteries have recently attracted much attention by using polyacetylene[1] and polyaniline[2] as electrode materials. In a search for other electrode materials, we found that commercially available activated carbon fiber (ACF)[3] could be used for battery and electric double layer capacitor.[4,5,6,7] Similar studies have also been reported by other groups.[8,9] This paper describes the charge-discharge characteristics and self-discharges of a Li-battery, Li | $LiClO_4$ in propylene carbonate (PC)| $(ACF^-)Li^+$, and electric double layer capacitor, $(ACF^-)Li^+$ |$LiClO_4$ in PC| $(ACF^+)ClO_4^-$.

EXPERIMENTAL

The Li-ACF battery and ACF-ACF capacitors were made in glass vessels. The details were described before.[6] PC solution of $LiClO_4$ (1 mol dm^{-3}) was used as an electrolyte solution. PC was dried in the presence of Li, then of molecular sieve, and finally vacuum distilled.

RESULTS AND DISCUSSION

Li-ACF Battery Below 3.0 V

We previously reported such Li-ACF battery as Li|$LiClO_4$ in PC|(ACF^+)-ClO_4^-,[4,5,6] and found the energy density to be comparable to the same type of polyacetylene battery. However, self-discharge was a serious problem owing to the high voltage (4 V). Thus, we now studied a battery, Li |$LiClO_4$ in PC| $(ACF^-)Li^+$, at the expense of energy and power densities. The redox potential of ACF itself is 3.0 V vs Li/Li^+. The charge-discharge curves of this cell was obtained between 3.0 V and 2.5 V, 2.25 V, or 2.0 V under constant current (0.1 ma/cm^2)[2,10], and are shown in Fig. 1. No plateau was observed. This is because the cathode reaction is mainly the formation of an electric double layer.

We found that the open circuit voltage increased gradually after having discharged to the voltages higher than 1.5 V. Figure 2 shows the recovery of V_{oc} after having discharged to 1.5 V. This is caused by an undoping of Li^+ from ACF, although the detailed mechanism is obscure. This battery could not be charged to 3.0 V after over-discharge below 1.5 V. About 200 Couloms of electricity per 1 g of ACF could be obtained when the cell was discharged from 3.0 V to 1.5 V.

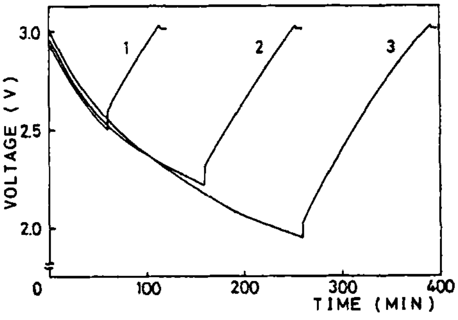

FIGURE 1 Charge-discharge curves of Li-ACF battery under constant current of 0.1 ma/cm^2.
(1) 3 V - 2.5 V; (2) 3 V - 2.25 V; (3) 3 V - 2.0 V.

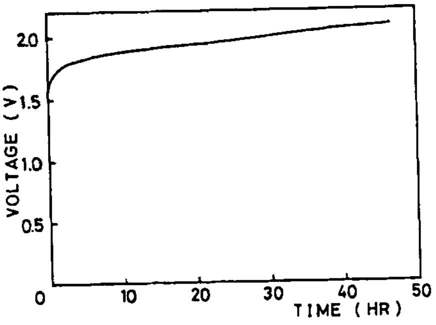

FIGURE 2 Recovery of an open circuit voltage with time after Li-ACF battery had been discharged to 1.5 V.

Self-discharge of Electric Double Layer Capacitor

To avoid the self-discharge of the electric double layer capacitor, $(ACF^-)Li^+ \mid LiClO_4$ in PC $\mid (ACF^+)ClO_4^-$, is one of the most crucial points. Figure 3 shows the self-discharge of the capacitor under various conditions as described in the figure caption after having charged to 2.0 V. About 90 percent of the self-discharge occurred at the negative electrode. The self-discharge curves consist of initial steep voltage drops followed by slow and almost linear voltage drops with time. Although these two voltage drops seem to be different in origin, we could not clarify them. Let us now compare the self-discharge by the time during which the cell voltage decreases by 1 V in the latter slow self-discharge process. Table 1 summarizes the self-discharge (hrs/V) thus obtained for the curves 1 - 5 in Fig. 3.

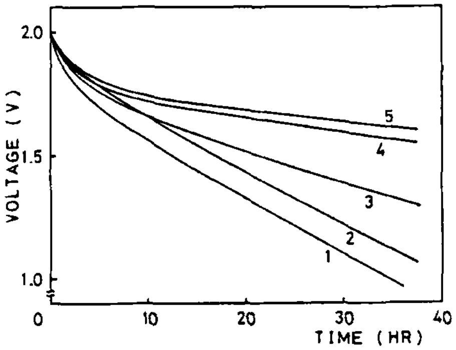

FIGURE 3 Self-discharge of ACF-ACF capacitor made under the following conditions. (1) nitrogen atmosphere; (2) dried aluminum was added to 1; (3) bubbled 1 with nitrogen gas; (4) dried aluminum was added to 3; (5) the cell was degassed by freeze-pump-thaw method.

TABLE I Self-discharge of ACF-ACF capacitors in Fig. 3.

Curves	Self-discharges (hrs/V)
1	50
2	52
3	111
4	200
5	333

The slight difference of the self-discharge of curve 1 from 2 arises from a trace of water in PC (probably 10 - 50 ppm), which can be eliminated by aluminum powder. The great suppression of the self-discharge in curve 3 shows that dissolved oxygen has a pronounced effect on the self-discharge. Although the self-discharge was suppressed uppermost under vacuum (curve 5),[11] it could not be removed completely. This may be attributed mainly to the reduction of PC at the negative electrode and/or some irreversible chemical reaction of dopants with ACF, both of which were also postulated as the main reasons for the self-discharge in polyacetylene battery. The presence of functional groups (about 1 meq/g) in ACF, such as OH and CO_2H, may also contribute to the self-discharge. For example, deprotonation from ACF results in the loss of positive charge.

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10. The ACF cloth (CH-20) has an apparent specific surface area of 100 cm^2/g. Since ACF has a fibril structure, and each fibril contains a large number of small holes (about 20 Å), the true specific surface area is extremely large (2000 m^2/g). However, the apparent surface area was used for the calculation of the current density for convenience.
11. The great suppression of the self-discharge under vacuum may arise from the desorption of gases from ACF, because ACF has a great adsorption ability of gases; ACF was manufactured for the adsorber of organic vapors in chemical factory in order to prevent air pollution. See, T. Kihata, T. Fukuda, N. Ishizaki, S. Ohmori, and H. Komagata, Kagaku Kogyo, 44, 343 (1980).