Acetylene black/poly(vinylidene fluoride) gel electrolyte composite electrode for an electric double-layer capacitor

Tetsuya Osaka *, Xingjiang Liu, Masashi Nojima

Department of Applied Chemistry, School of Science and Engineering, Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan

Abstract

A composite electrode with carbon powder and poly(vinylidene fluoride) (PVdF) gel electrolyte is prepared and investigated as an electrode for an electric double-layer capacitor (EDLC). PVdF-based gel, with a mixture of ethylene carbonate (EC) and propylene carbonate (PC) as plasticizer, and tetraethylammonium tetrafluoroborate (TEABF$_4$) is used as the electrolyte of the EDLC. The composite electrode shows a higher specific capacitance and lower ion-diffusion resistance inside the electrode than those studied previously with carbon electrodes prepared with PVdF binder only. The highest specific capacitance, 4.1 F g^{-1}, is achieved for an acetylene black (AB)/PVdF gel composite electrode with a PVdF content of 30 wt.%. This is because the electrode has the best contact state between AB and PVdF gel electrolyte. Finally, the performance of an EDLC with AB/PVdF gel composite electrodes is evaluated and an excellent cyclability over 10^5 cycles with ∼ 100% coulombic efficiency is achieved during charge–discharge between 1.0 and 2.0 V at 1.66 mA cm^{-2}. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

The electric double-layer capacitor (EDLC) can be discharged at high current density with a high-rate response. Thus, it is attractive as a rechargeable pulse-power source for electric vehicles and electronic devices [1–5]. To fabricate an EDLC with high energy and high power density, using a thin layer electrolyte is one of the effective methods [6]. We have been attempted to use polymer-based or polymer gel electrolytes with stability in a wide potential range to achieve this objective [6–8]. The gel electrolyte, which consists of polymer matrix that supports the electrolyte and the organic solvent, possesses a high ionic conductivity of approximately 10^{-3} S cm^{-1} at ambient temperature, which is close to that of an organic solvent electrolyte. It has acceptable mechanical strength close to that of a solid polymer electrolyte (SPE) [8–11]. Therefore, the gel electrolyte has properties superior to those of an SPE and an organic solvent electrolyte and can be used in thin film capacitors [6,8,12–15] and lithium secondary batteries [9–11,16–23] for operation at ambient tempera-

ture. Poly(ethylene oxide) (PEO), poly(methylmethacrylate) (PMMA), poly(acrylonitrile) (PAN) and poly(vinylidene fluoride) (PVdF)-based gel electrolytes have been investigated and applied to EDLC [6–8,13–15]. Among them, the PVdF-based gel electrolyte is notable since it has a higher ionic conductivity, excellent electrochemical stability, stronger mechanical strength, and combustion-resistant properties [15,24].

In our previous study, flat isotropic high-density graphite (HDG) with high surface area was found to be suitable as an electrode material in a thin EDLC using a SPE or a gel electrolyte [6–8]. When used as the electrode material of all-solid-state EDLC, however, the flat HDG tablet does not provide effective contact with the bulk electrolyte. By having the electrolyte inside the electrode, the contact surface area between electrode and electrolyte can be increased and the capacitance enhanced. This can be achieved by using a composite electrode made from active-material powder and gel electrolyte. Recently, a composite electrode with a gel electrolyte has been studied as a battery cathode or anode [25–27], while there have been no reports of its application in an EDLC. In this work, we investigate the possibility of fabricating an all-solid-state

* Corresponding author.

capacitor by using composite electrodes with PVdF gel electrolyte.

2. Experimental

2.1. Electrochemical cell

Various carbon materials were examined as electrode base materials, namely: HDG (specific surface area: 0.809 m^2 g^{-1}; pore diameter: 0.42 μm; in bulk specific gravity: 1.90 g cm^{-3}; supplied by Toyo Tanso); highly-graphitized mesocarbon microbeads (MCMB-28: particle size = 1–20 μm; 2800°C heat treatment; supplied by Osaka Gas, Japan); less highly-graphitized mesocarbon microbeads (MCMB-7: particle size = 1–20 μm; 700°C heat treatment; supplied by Osaka Gas); acetylene black (AB: particle size = 2–3 μm; supplied by Osaka Gas). Electrodes were formed by mixing the above carbon powders with various amounts of PVdF (from 5 to 75 wt.%) as a binder. The resulting mixture was pressed on to a porous nickel substrate to form a pellet (diameter = 1.24 cm). To make the gel polymer electrolyte, PVdF (molecular weight: 534 000 g mol^{-1}; supplied by Aldrich Chemical) was used as the base material and was combined with a plasticizer comprising a mixture of ethylene carbonate (EC; supplied by Mitsubishi Chemical) and propylene carbonate (PC; supplied by Mitsubishi) and $TEABF_4$ or $TBABF_4$ as the supporting electrolyte. The chemical composition (molar composition) of the gel electrolyte was PVdF: PC: EC: $TEABF_4$ or $TBABF_4$ = 30: 19: 48.5: 2.5.

The cell was constructed from a pair of the above electrodes and a PVdF gel electrolyte film in an argon glove box.

2.2. Preparation of gel electrolyte and composite electrode

The PVdF gel electrolyte was prepared as follows. A $TEABF_4$ (or $TBABF_4$)/PC + EC mixture was first prepared at 40–50°C. Dry PVdF powder was added to this mixture with stirring. The PVdF-based gel electrolyte film was obtained by casting a *N*-methyl-2-pyrrolidinone (NMP) solution of the PVdF-based mixture (10 mg/ml) on to a glass petri dish and heating at 100°C in glove box for more than 4 h. The thickness of the films was controlled within the range of 50 and 500 μm by varying the quantity of the casting mixture. The gel electrolyte films thus prepared were kept in glove box under an argon atmosphere.

Fig. 1 shows the preparation procedure of the composite electrode. First, the carbon/PVdF was mixed with PC + EC + $TEABF_4$ (or $TBABF_4$)/NMP solution, then the carbon slurry was cast on to a porous nickel substrate and heated at 100°C for about 2 h to form a carbon/PVdF gel composite layer, finally, the layer was pressed at about 300
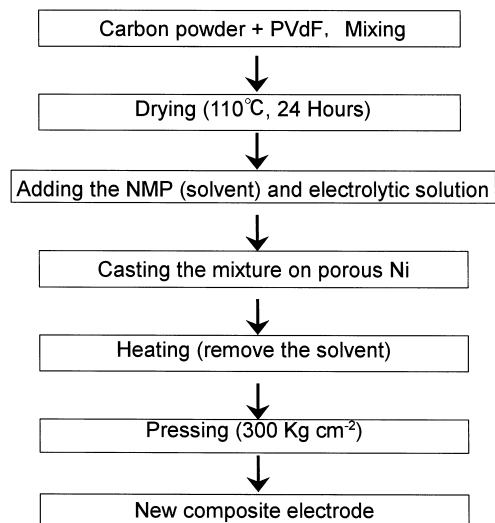

Fig. 1. Preparation process of composite electrode.

kg cm^{-2} to obtain a carbon/PVdF gel composite electrode sheet of about 200 μm.

2.3. Measurement methods

Electrochemical measurements were performed by using a sandwich-type cell in a glove box at ambient temperature. Cyclic voltammetric measurements of the cell were made in the potential range -4.5 to 4.5 V. The potential scan rate was 20 mV s^{-1}. The AC impedance spectroscopy was measured at an open-circuit potential in the frequency range 20 kHz to 5 mHz. The capacitor was charged and discharged between 2.0 and 1.0 V at a constant current of 1.66 mA cm^{-2}. The leakage current test was performed at a float potential of 2.0 V, and the self-discharge curves were recorded after charging at 1.66 mA cm^{-2} to 2.0 V. All electrochemical measurements were performed at ambient temperature.

An optical microscope was employed to characterize the contact state between carbon particles and the PVdF gel electrolyte.

3. Results and discussion

3.1. Carbon-based composite electrode

In our previous investigations [6–8], we confirmed that the HDG electrode with an appropriately roughened surface has a higher specific capacitance in SPE or gel electrolyte. On the other hand, many researchers have verified that $TEABF_4$ is a good supporting salt for use in an EDLC [13,14]. We compared only the effect of $TEABF_4$ and $TBABF_4$ on ionic conductivity and capacitance by using an HDG electrode. As shown in Table 1, $TEABF_4$ has a more beneficial effect on capacitance and ion conductivity characteristics than $TBABF_4$ which correlates

Table 1
Ion conductivity of various gel electrolytes and capacitance of HDG electrode in PVdF gel electrolyte with different supporting salts at ambient temperature

Gel electrolyte	PVdF	
Supporting electrolyte	$TBABF_4$	$TEABF_4$
Conductivity (10^{-3} S cm^{-1})	1.46	2.35
Capacitance (mF cm^{-2})	11	14.7

Table 2
Capacitance of various electrodes (with or without gel) in PVdF gel electrolyte at ambient temperature

Electrode base material		MCMB-7	MCMB-28	AB
Capacitance (mF cm^{-2})	with PVdF	5.85	7.22	27.4
	with PVdF gel	12.6	15.7	47.6
Capacitance (mF g^{-1})	with PVdF	156	144	1270
	with PVdF gel	270	262	2560

with ion size (geometric size: $TEA^+ < TBA^+$) [14]. Thus, we have used $TEABF_4$ as the supporting salt for PVdF gel electrolyte.

To obtain a high electric energy, it is important for the capacitor to have a wide working potential range and a high electrode capacitance. Various carbon materials have been studied as EDLC electrodes; the specific capacitance is affected by carbon crystal structure. Three types of carbon powders are selected in this study, namely, highly-graphitized MCMB-28, less highly-graphitized MCMB-7 [28], and amorphous AB powder. The capacitance and the electrochemical stability are compared as follows. First, the double-layer potential range is, of course, limited by electrode and electrolyte interaction, and is strongly affected by the chemical or electrochemical stability of the electrode and the electrolyte media. The working potential range of various carbon electrodes has been evaluated by cyclic voltammetry measurements. Fig. 2 shows cyclic voltammograms obtained with EDLCs with various electrodes in PVdF gel electrolyte. The results show that there is good capacitor performance over 3.0 V for carbon electrodes, and that the Ni electrode has a stable potential range of 4.3 V. The comparatively narrow stable potential range of carbons is attributed to the decomposition of PC solvent. Thus, the cut-off potential of the capacitors was set below 3.0 V.

To improve further the effective contact surface between the electrode and the polymer gel electrolyte, poly-
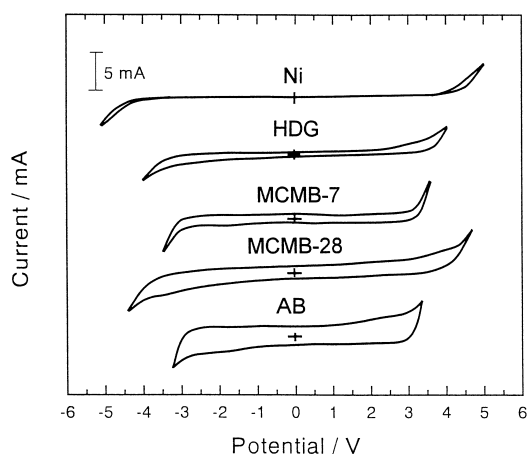
mer gel electrolyte was used as a binder for the carbon powder electrode (composite electrode). The specific capacitances of various carbon powder electrodes with PVdF only or PVdF gel electrolyte binder are compared in Table 2. The capacitances were measured by AC impedance responses at open circuit potential. It can be seen that the capacitance of the electrode is greatly increased by using the gel electrolyte binder, with respect to either electrode surface or weight. When PVdF gel electrolyte is used as the binder, the contact surface area between the carbon powder and electrolyte is improved, and thus, a capacitance enhancement is observed. The AB/PVdF gel electrolyte composite electrode gives the highest capacitance. This may be due to the small particle size of AB compared with other carbon powders. Therefore, AB was examined as the base material for the composite electrode.

The AC impedance responses of AB electrode capacitors and MCMB-7 electrode capacitors are shown in Fig. 3. The Cole–Cole plots of capacitors with PVdF binder and PVdF gel electrolyte binder show a typical response for a porous electrode [29]. An initial 45° line in the high-frequency region was obtained with each capacitor. This is due to ion diffusion in the inside of the electrode. As shown in Fig. 3a,b, the ion diffusion inside the electrode results in a rapid decrease in resistance for the composite electrode with PVdF gel electrolyte binder compare with an electrode with PVdF binder only. The difference in diffusion resistance between the composite electrode (AB or MCMB-7/PVdF gel electrolyte) and the electrode (AB or MCMB-7/PVdF binder) is believed to be due to the difference in the quantity of the ion-conducting phase. The composite electrode with gel electrolyte binder can provide a sufficient ion-conducting phase inside of the electrode to give a high capacitance and a low ion-diffusion resistance. In the case of electrode using PVdF binder only, only a few ion-conducting phases leak from the gel electrolyte film to enter the inner electrode [8]. Therefore, a higher ion-diffusion resistance is obtained.

3.2. Optimization of content of PVdF gel electrolyte as binder of AB composite electrode

According to the above results, we found that the AB/PVdF gel composite electrode has the highest capacitance of the carbon electrodes that have been studied.

Fig. 2. Cyclic voltammograms of various electrodes at 20 mV s^{-1} in PVdF gel electrolyte at ambient temperature.
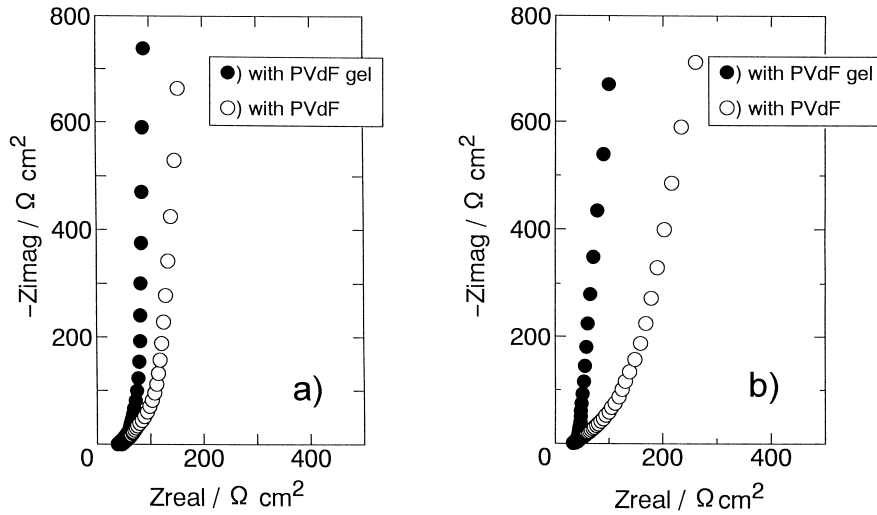
Fig. 3. Cole–Cole plots for capacitors with: (a) AB electrode, with or without PVdF gel electrolyte; (b) MCMB-7 electrode, with or without PVdF gel electrolyte (f: 20 kHz to 5 mHz).

Therefore, we investigated the optimum ratio of AB and gel electrolyte. Fig. 4 shows the Cole–Cole plots of EDLCs using AB composite electrodes as a function of various contents of PVdF gel electrolyte binders. The full-scale plot (Fig. 4a) shows a typical capacitor impedance response. A semicircle is obtained for an AB/PVdF gel composite electrode when the PVdF content is 75 wt.%, as shown in Fig. 4b. This may be caused by the contact resistance and the geometric capacitance. Also, if a large quantity of PVdF is mixed into the composite electrode, the contact state between the AB particles becomes poor and, thus, a large contact resistance appears. Optical mi-crographs are shown in Fig. 5 to illustrate the composite electrode state as a function of PVdF content. With 75 wt.% PVdF (Fig. 5d), the AB blocks are completely separated by PVdF gel electrolyte, and the state corre-sponds exactly to the results in Fig. 4, showing a semicir-cle in the high frequency region of Cole–Cole plot. With 50 wt.% PVdF, the gel electrolyte islands have white parts of composite electrode (Fig. 5c), and this results in the poor contact state between AB particles. By contrast, a homogeneous mixture of AB/PVdF gel electrolyte was achieved when the PVdF content of the AB composite electrode is less than 30 wt.% in Fig. 5a,b. Furthermore, we can calculate the capacitance of the composite elec-trode from the AC impedance response in the lower fre-quency region using Eq. (1) [30].
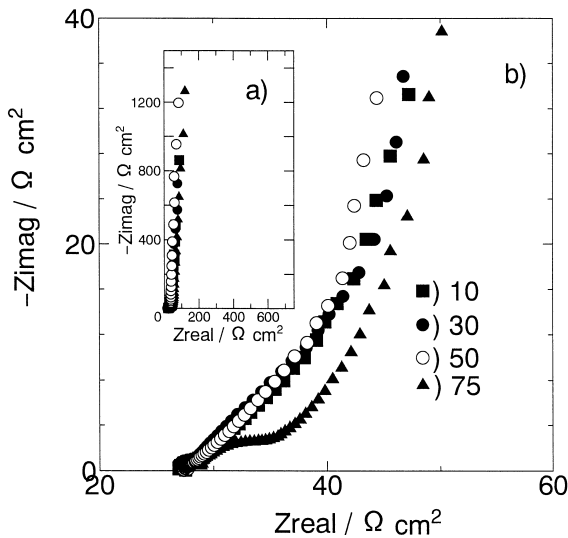
$$C = -2\left(Z_{\mathrm{imag}} \times \omega\right)^{-1} \tag{1}$$

where C, Z_{imag} and ω are the capacitance of the electrode, the imaginary component, and the angular frequency, re-spectively. The capacitances are expressed as F g^{-1} (AB mass) and mF cm^{-2}. The results are summarized in Fig. 6. Maximum capacitance is achieved in an AB composite electrode with 30 wt.% PVdF in terms of both mass specific capacitance and surface-area specific capacitance. This suggests that the composite electrode has the best contact surface between the AB and the PVdF gel elec-trolyte at this mixing ratio. The composite electrode has a volume resistivity in the order of 10^{-3} to 10^{-4} Ω cm. Therefore, the AB composite electrode with the optimized PVdF content (30 wt.%) was used for an EDLC applica-tion.

Fig. 4. Cole–Cole plots of cells with AB/gel composite electrodes: (a) full scale; (b) high frequency region.

(a). 10% PVdF

(b). 30% PVdF

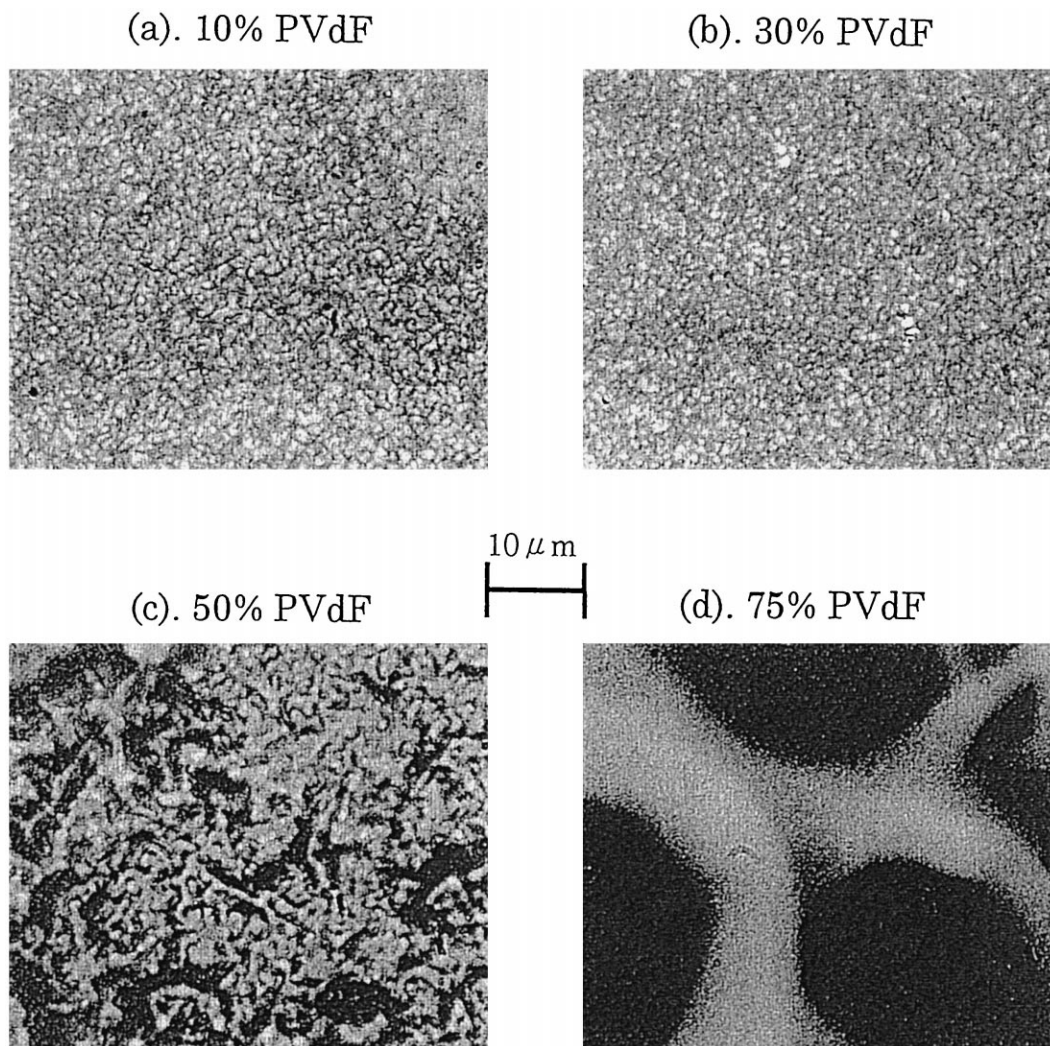### (c). 50% PVdF

$10\,\mu\mathrm{m}$

(d). 75% PVdF

Fig. 5. Optical micrographs of composite electrode of AB with various contents (wt.%) of PVdF.

3.3. Capacitor characteristics

Fig. 7 shows the charge–discharge curves of a coin-type capacitor with an AB composite electrode and a PVdF gel electrolyte at ambient temperature. Cycling was carried out between 1.0 and 2.0 V at 1.66 mA cm^{-2}. This capacitor shows the typical charge–discharge performance of an EDLC at the 10th cycle and even at the 50 000th cycle.
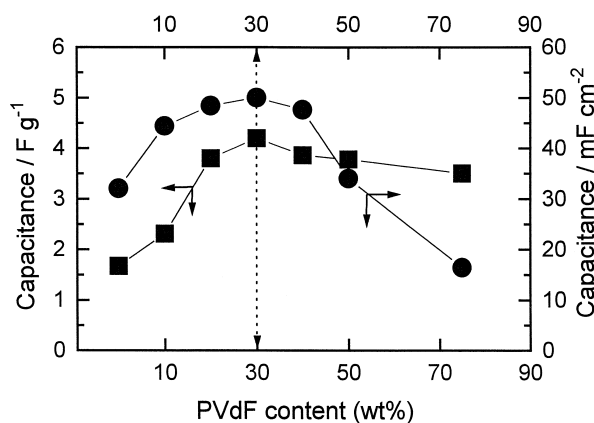
Fig. 6. Dependence of PVdF content on capacitance of an AB composite electrode. The capacitance is calculated from AC impedance measurements.
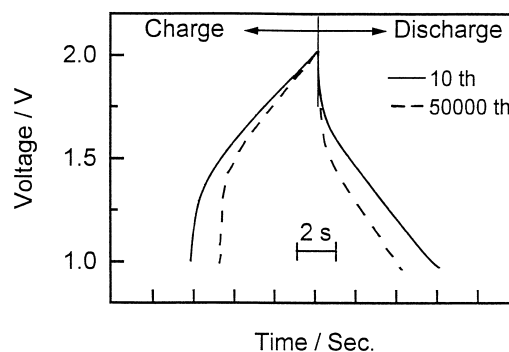
Fig. 7. Charge–discharge curves at 1.66 mA cm^{-2} for an EDLC using AB composite electrodes and PVdF gel electrolyte at ambient temperature.
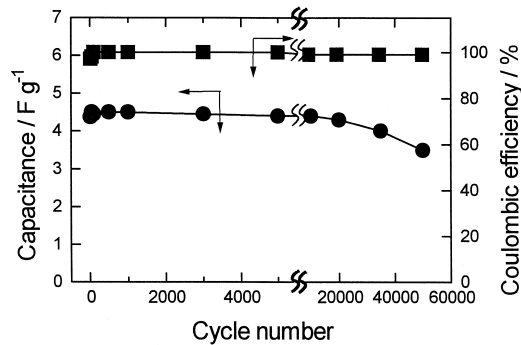
Fig. 8. Stability of capacitance and coulombic efficiency with number of cycles of a coin-type capacitor with an AB composite electrode (30 wt.% PVdF) and a PVdF gel electrolyte (charge–discharge current: 1.66 mA cm^{-2}).

The charge or discharge capacitance and coulombic efficiency of the capacitor are determined by the following equations. The results are plotted in Fig. 8.

Capacitance: $C = (I \times t)/\Delta E$ (2)

Coulombic efficiency: $\eta = (t_D/t_C) \times 100$ (3)

In Eq. (2), C, I, t and ΔE (or dE) are the capacitance, charge or discharge current, charge or discharge time, and potential difference, respectively. In Eq. (3), t_D and t_C is the time for discharging and charging, respectively. Fig. 8 shows that this coin-type capacitor is very stable in capacitance and coulombic efficiency (about 100%) over 10^4 cycles, even if it is cycled over 10^5 cycles. The leakage current is less than 3 μA cm^{-2}. The slow decreases in capacitance with cycling over 10^4 cycles may be due mainly to the organic electrolyte phase separating from the PVdF phase, which causes an decrease in ion conductivity of the PVdF gel electrolyte film. This phase separation effect is also apparent in the charging–discharging process, and it gives a large IR drop at the 50 000th cycle, as shown in Fig. 7. Finally, the self-discharge of the EDLC with the AB composite electrode was measured and, as shown in Fig. 9, this EDLC displays good retention of potential.
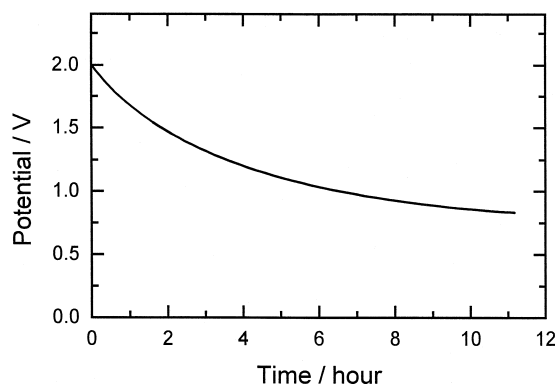

Fig. 9. Self-discharge characteristic of capacitor using AB composite electrodes (30 wt.% PVdF) and PVdF gel electrolyte after charging to 2.0 V.

4. Conclusions

A carbon powder/PVdF gel electrolyte composite electrode has been prepared as an electrode for an EDLC. It is found that the new composite electrode has a higher specific capacitance and lower ion-diffusion resistance than a carbon electrode with a PVdF binder only. The AB composite electrode exhibits the highest capacitance because of the small particle size. The capacitance of the AB composite electrode depends strongly on the content of the PVdF gel electrolyte binder. The maximum capacitance of 4.1 F g^{-1} is achieved in an AB composite electrode with 30 wt.% PVdF, which was about 30 times larger than that of the HDG electrode. Because the electrolyte is introduced into inner electrode, the contact area between electrode and gel electrolyte is increased. The best contact state is obtained at 30 wt.% PVdF content. An EDLC with an AB composite electrode and a PVdF gel electrolyte gives excellent cyclability performance (over 10^5 cycles) with a low leakage current and good potential retention.

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