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Short communication

Application of activated carbon/DNA composite electrodes to aqueous electric double layer capacitors

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ABSTRACT

A novel capacitor electrode auxiliary, deoxyribonucleic acid (DNA), is applied to an electric double layer capacitor (EDLC) containing an aqueous 3.5 M NaBr electrolyte. The present electrode is composed of activated carbon (95 wt.%) and DNA (2.5 wt.%) with polytetrafluoroethylene (PTFE) as a binder (2.5 wt.%). An EDLC cell with the DNA-loading electrodes exhibits improved rate capability and discharge capacitance. An EDLC cell with DNA-free electrodes cannot discharge above a current density of 3000 mA g^{-1} (of the electrode), while a cell with the DNA-loading electrodes can work at least up to 6000 mA g^{-1}. Moreover, an open-circuit potential (OCP) of the DNA-loading electrode sifts negatively with ca. 0.2 V from an OCP of the corresponding electrode without DNA. It is noteworthy that a small amount of DNA loading (2.5 wt.%) to the activated carbon electrode not only improves the rate capability but also adjusts the working potential of the electrode to a more stable region.

1. Introduction

Electric double layer capacitors (EDLCs) have been investigated by many researchers for power supply application to vehicles because such application is expected to develop a great market. The energy storage mechanism of EDLCs is essentially based on an electric double layer (EDL) formed at an electrode/electrolyte interface. EDLC is a clean, simple energy storage system because the charge–discharge of electric energy proceeds without a faradic reaction. This contributes to its long cycle life and high power density when compared to conventional rechargeable batteries.

As for active materials applicable to EDLC electrodes, capacitor researchers have focused on various carbon materials, i.e., low crystalline carbon: activated carbon fiber cloth [1–3], carbon aerogel [4,5], activated carbon powder [6,7], and carbon formed from pyrolyzed organic polymers [8,9]; as well as high crystalline carbon: carbon nanotube [10,11], graphite [12], carbon black [13], and fullerene-type carbon [14]. Generally, carbon materials for EDLC electrodes should have a large specific surface area as well as chemical stability providing their long cycleability [15].

On the other hand, concerning EDLC electrolytes, there have been variations such as aqueous [2,16], organic [17], ionic liquid [18], and gel [3,19,20] electrolytes. Although the decomposition voltage of aqueous electrolytes (the theoretical decomposition voltage is 1.23 V at pH 7) is lower than that of organic electrolytes, the electric conductivity of aqueous electrolytes is much higher (typically one order of magnitude) than that of organic electrolytes for EDLC [18]. EDLCs utilizing an aqueous electrolyte system have attracted great interest because they exhibit higher safety, higher specific capacitance and higher power density when compared to EDLCs with any other electrolyte systems.

Generally, however, most carbon materials show high resistance in aqueous electrolytes because carbon materials have insufficient affinity for aqueous electrolytes. Moreover, fluoropolymer, e.g., polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVdF), as well as styrene-butadiene rubber as a binder, is necessary for EDLC electrodes with carbon powder to keep the electrode shape. Such binders for EDLC electrodes also have poor affinity for aqueous electrolytes. Thus, a serious problem arises: there is a considerable resistance at the electrode/electrolyte interface in an aqueous EDLC. To solve this problem, some researchers have applied surface treatment to electrodes in an attempt to enhance their affinity for an aqueous electrolyte and hence decrease electrode/electrolyte interface resistance, e.g., electrochemical treatment [21,22].

In our preliminary study, we optimized an electrode/electrolyte interface resistance for an aqueous EDLC system by loading a small amount of deoxyribonucleic acid (DNA) as a hydrophilic auxiliary into an activated carbon electrode [23]. We found that the hybridized electrode exhibits enhanced capacitance in neutral aqueous electrolytes, e.g., concentrated NaBr and NaCl aqueous

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electrolytes, after testing various electrolytes ranging from a strong base to a strong acid. However, rational origins of the improved EDLC performance by the DNA loading to an activated carbon electrode remain to be elucidated.

In this work, we performed electrochemical characterization of a DNA-loading electrode for EDLC with an aqueous 3.5 M NaBr electrolyte. The aim of this study is to elucidate the effect of DNA on EDLC performance, focusing on each electrode (positive and negative) behavior. Our findings are that a small amount of DNA loaded to an activated carbon electrode enhances the rate capability of the electrode because of a decrease in an ionic diffusion resistance in the electrode interior; moreover, the presence of DNA improves the electrode's coulombic efficiency due to the shift of the electrode working potential to a more stable potential region, i.e., the negative shift of the electrode open-circuit potential (OCP) by the DNA presence in the electrode interior.

We used DNA extracted from salmon testes for our electrode preparation. Accumulated salmon testes abstracted from salmon bodies approaches 7500–12,500 ton per year in Japan. However, quite a limited amount of that accumulation has been used for industry such as food products and cosmetics; most of the salmon testes have been thrown away as industrial waste, causing an environmental problem. In this context, recently, some researchers have focused their interest on DNA extracted from industrial waste for varied application [24,25]. In a positive sense, DNA abstracted from salmon testes is cheap, and the application of DNA to mass-produced devices such as EDLC may be a desirable process with the object of effective utilization of industrial waste.

2. Experimental

We used single-strand DNA as sodium salt (Na-DNA, Daiwa Fine Chemicals Co., Ltd., mean molecular weight: ca. 10^6), which is mass-produced DNA from salmon testes as industrial waste. DNA-loading electrodes were prepared by mixing 20 mg of activated carbon powder (BCP, supplied by Toyobo Co, BET specific surface area: 940 $m^2\,g^{-1}$, particle size: ~5 μm in mean diameter, pore size: ~2.8 nm in mean diameter) as active material with 2.5 wt.% polytetrafluoroethylene (PTFE, Daikin Industries F-104) as binder together with 2.5 wt.% DNA; we used PTFE binder because it provides high mechanical strength to the electrode and is effective even in small amounts. Thereafter, the resulting composite was pressed onto a Ni gauze (Nilaco, 100 mesh) as a current collector. The obtained composite electrodes were approximately 400 μm thick and 10 mm in diameter. Activated carbon and PTFE electrodes without DNA were also prepared for comparison. The surface morphology of DNA-loading electrodes was observed using a scanning electron microscope (SEM, JEOL JSM-6700).

Before assembly of EDLC cells, the electrodes and a piece of glass-fiber filter paper (ADVANTEC GB-100R) as a separator were immersed in an electrolyte, typically 3.5 M NaBr aqueous solution, for 3 h under a reduced pressure. Two types of EDLC cell were used in this study: (i) a two-electrode symmetric cell with a Teflon case was fabricated with a pair of the composite electrodes and a separator, (ii) a two-electrode symmetric cell connected with another cell containing a reference saturated calomel electrode (SCE).

We performed constant-current discharge following charging at a constant current combined with a constant voltage (CC–CV) method using the two-electrode symmetric cell. In detail, the charge–discharge procedure can be divided into four periods. First, the EDLC cell was charged to 0.8 V at a constant-current density of 100 mA g^{-1}. Next, the cell was kept at 0.8 V for 200 s, and then the cell was discharged to 0.0 V at various constant-current densities, 50–6000 mA g^{-1}. Finally the cell was kept at 0.0 V for 1000 s so that residual electric charge in the electrodes could be eliminated. The cell performances were evaluated using a Solartron SI 1287A electrochemical interface. We also used the two-electrode cell together with an outside reference electrode to evaluate the polarization characteristics of positive and negative electrodes, respectively, using a Solartron 1480 Multi Stat. Using this cell, the positive and negative electrode potentials vs. SCE were monitored when the cell was charged to 0.8 V and discharged to 0.0 V at a current density of 100 mA g^{-1}.

Before the present electrochemical measurements, 50 formation cycles were carried out at a current density of 100 mA g^{-1} because the as-prepared electrodes have a high electrode/electrolyte resistance. All experiments were performed at a room temperature of 25 °C.

3. Results and discussion

SEM images of surface morphology for DNA-loading and DNA-free electrodes are shown in Fig. 1(a) and (b), respectively. No critical difference is observed between these electrodes, irrespective of DNA presence, which mainly contain activated carbon and a relatively low amount of PTFE forming a three-dimensional open network composed of activated carbon interfaces. The results mean that a small amount of DNA addition (2.5 wt.%) can hardly affect the electrode morphology. Moreover, no obvious difference in the specific surface area and pore size distribution between the electrodes with and without DNA is observed, suggesting that the presence of DNA does not affect pore structure at the activated carbon.

Charge–discharge tests of these electrodes were performed with the two-electrode symmetric cell. Activated carbon as well as PTFE has insufficient affinity for an aqueous electrolyte. Therefore, charging by a constant current (CC) method may result in a low charge level in pores at the electrodes. To ensure a full charge, we applied a CC–CV method to charging. Fig. 2 shows discharge capacitance of the present electrodes with and without DNA as a function of current density in 3.5 M NaBr electrolyte. The discharge capacitance of

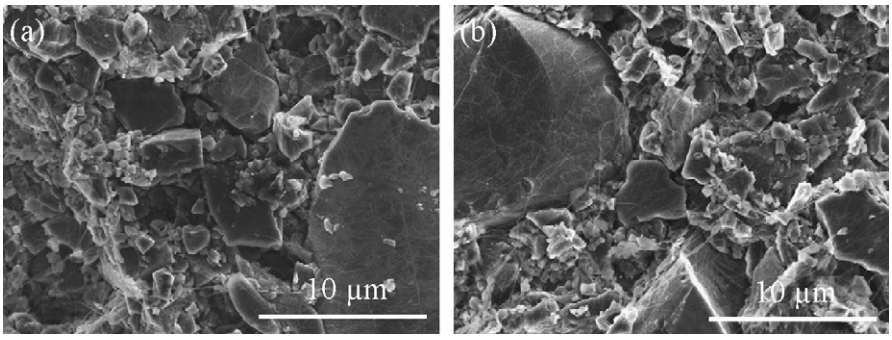

Fig. 1. SEM images of surface morphology: (a) DNA-loading electrode and (b) DNA-free electrode.

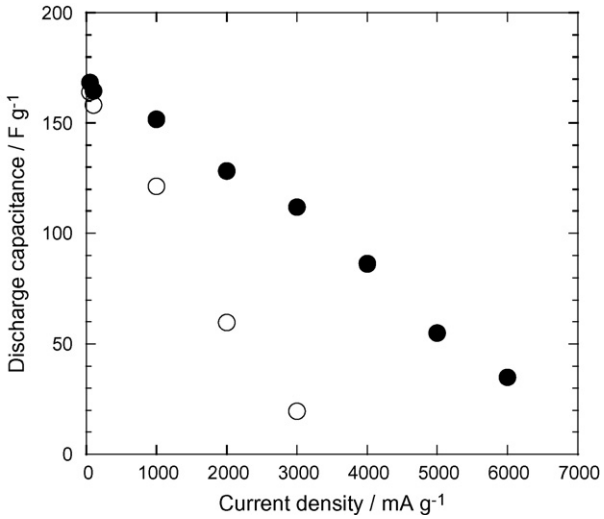

Fig. 2. Relationship between discharge capacitance and current density for EDLC cells containing DNA-loading electrodes (●) and DNA-free electrodes (○) with 3.5 M NaBr electrolyte.

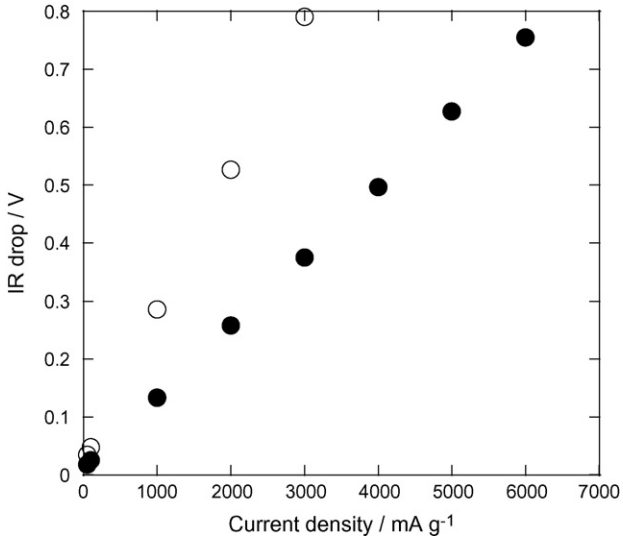

Fig. 3. *IR* voltage drop of EDLC cells based on DNA-loading electrodes (●) and DNA-free electrodes (○) with 3.5 M NaBr electrolyte as a function of current density.

the electrodes C is calculated according to

$$C = (2 \times I \times t)/(w \times \Delta E) \quad (1)$$

where I is the discharge current, t the discharge time, w the mass of active material at an electrode, and ΔE the voltage variation in discharging, excluding *IR* voltage drop.

At relatively low current densities of 50 and 100 mA g^{-1}, the discharge capacitances of the electrodes with and without DNA are similar. This suggests that the effect of DNA loading to the electrode on its capacitance is almost negligible at quite low current densities. However, the discharge capacitance of the DNA-loading electrode is much higher than that of the DNA-free electrode with the higher current densities; at a current density of 3000 mA g^{-1}, the discharge capacitance of the DNA-loading electrode (119.9 F g^{-1}) is about six times larger than the electrode without DNA (19.4 F g^{-1}). Furthermore, the electrode without DNA cannot discharge at all above a current density of 3000 mA g^{-1}, while the DNA-loading electrode can work at least up to 6000 mA g^{-1}, where it still can generate 34.9 F g^{-1}.

The *IR* (voltage) drop of the EDLC cells is estimated from discharge curves with various current densities and is shown in Fig. 3. The *IR* drop of a DNA-loading electrode is approximately half that of the DNA-free electrode at and below a current density of 3000 mA g^{-1}. Linearity relevant to Ohm's law is observed for electrodes both with and without DNA (Fig. 3). This means that a major resistance of EDLCs is derived from a constant resistive component existing inside the electrodes. Therefore, one can see that the presence of DNA can reduce the internal resistance of the electrode.

To evaluate polarization characteristics of positive and negative electrodes, we used the two-electrode cell connected to an outside reference electrode. Fig. 4(a) shows the charge–discharge voltage curves at a current density of 100 mA g^{-1}; this voltage corresponds to a potential difference between negative and positive electrodes. The charge–discharge curve of the DNA-loading electrode shows an ideal linearity with a gentler gradient and a smaller *IR* drop than that of a DNA-free electrode. This means that the charge–discharge capacitance for the DNA-loading electrode is stable or invariable within the operating voltage and is larger than that of the DNA-free electrode, while a charge profile of the DNA-free electrode is non-ideal, i.e., seems composed of two positions with different slopes.

The charge–discharge coulombic efficiency of the DNA-free and DNA-loading electrodes at this current density are evaluated as 74 and 94%, respectively. The loss of the efficiency may be attributed to some faradic reaction, e.g., electrolyte decomposition, and to self-discharge, which is generally inevitable in non-faradic charge storage such as at a charged EDLC electrode. Because self-discharge becomes more ignorable with shorter duration, one can expect that a high current density, which corresponds to prompt

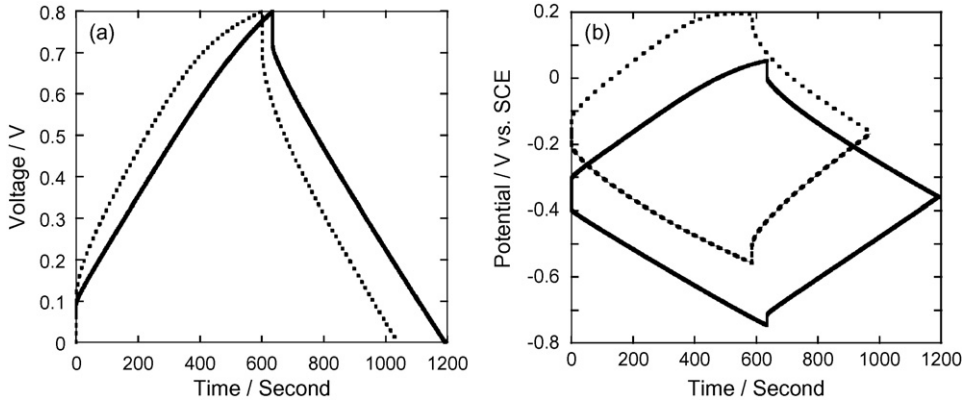

Fig. 4. Voltage or potential vs. time curves during galvanostatic cycles of EDLC cells based on DNA-loading electrodes (—) and DNA-free electrodes (····) with 3.5 M NaBr electrolyte at 100 mA g^{-1}; (a) voltage between positive vs. negative electrodes, (b) potentials of positive and negative electrodes vs. SCE.

charge–discharge in the same voltage range, reduces self-discharge effect, and hence an improved coulombic efficiency, unless there is an irreversible faradic process. In fact, when high current densities (>500 mA g^{-1}) are applied, the coulombic efficiency of the DNA-loading electrode is significantly improved; e.g., it becomes almost 100% at 1000 mA g^{-1} or above. However, the efficiency of the DNA-free electrode remains low even at such high current densities. These results suggest that the DNA-loading electrode essentially has reversible characteristics without an undesirable, faradic degradation process.

To understand each electrode behavior during the cycling shown in Fig. 4(a), potential variation of both the positive and negative electrodes vs. an external SCE was recorded as shown in Fig. 4(b). An open-circuit potential (OCP) of the DNA-loading electrode sifts negatively with ca. 0.2 V from an OCP of the electrode without DNA. This suggests that DNA loading to the electrode increases negative charges inside the electrode, probably because of the presence of negative charges in nucleotides (counter cation-free, H-form) constituting DNA, hence more negative OCP.

Moreover, the charge curve for the DNA-free positive electrode levels off near the end of charging, 0.2 V, while the other charge curves, for the DNA-free negative electrode as well as for the DNA-loading positive and negative electrodes, are essentially linear and have no obvious plateau position. This suggests that a faradic reaction would be involved in the charging process for the positive electrode without DNA, while a typical non-faradic charging (EDL charging) reaction proceeds at the DNA-free negative electrode as well as at DNA-loaded positive and negative electrodes. Therefore, one can ascribe a bend in the charge curve without DNA, shown in Fig. 4(a), to the plateau in the charge curve for a DNA-free positive electrode, which would be caused by a faradic reaction, e.g., electrolyte decomposition. Such a reaction should occur when an operating potential of an electrode exceeds the limit of a stable potential window; in the present study, the positive electrode without DNA would reach the higher limit of the stable potential window, and hence would level off.

Consequently, we can enjoy the benefit of DNA loading to the EDLC electrode; ca. 0.2 V negative shift of the electrode OCP by DNA loading can change the working potential of the positive electrode from a critical potential region to a more stable one as shown in Fig. 4(b). Although the working potential of the negative electrode also shifts negatively with 0.2 V with DNA loading, this electrode can still remain in a stable potential region as can be seen in Fig. 4(b); the charging profile of the negative electrode is still linear with DNA. This should be the origin of a large *IR* drop for the DNA-free system shown in Fig. 3.

4. Conclusion

A slight amount (2.5 wt.%) of DNA loading to the activated carbon electrode can provide high-rate capability as well as ideal voltage behavior for EDLC cells with 3.5 M NaBr electrolyte. The improvement with the DNA addition originates from: (i) a decrease in ionic (mainly anionic) diffusion resistance, (ii) negative OCP shift toward a stable potential region where a linear potential change of the electrode occurs with charging. Additionally, the present EDLC with the DNA-loading electrodes is inexpensive and quite safe; DNA used here from industrial waste is cheap, and the applied electrolyte is almost neutral, not strong acid or base.

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