Activated Carbon/DNA Composite Electrodes for Electric Double Layer Capacitors with Neutral Aqueous Electrolytes

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A novel electrode composed of activated carbon and DNA together with fluorinated binder has been prepared for an electric double layer capacitor (EDLC) with aqueous electrolytes. The DNA-loaded electrodes improve the rate capability and discharge capacitance of EDLC containing aqueous, neutral salt electrolytes. In contrast, the DNA-composite electrodes have a poor effect on the capacitance enhancement in acidic or basic electrolytes. The enhancement of discharge capacitance is significant especially at high-rate cycling in neutral salt electrolytes, because the presence of DNA reduces the internal resistance of an electrode and hence improves its rate capability.

Key Words: Electric Double Layer Capacitor (EDLC), DNA, Aqueous Electrolyte, Activated Carbon

1 Introduction

A considerable effort has been devoted to the development of electric double layer capacitors (EDLCs) for power-supply application especially on vehicle. Among various electrolytes for EDLCs, e.g., organic, aqueous, and gel electrolytes, an aqueous electrolyte system provides particular advantages; EDLCs containing an aqueous electrolyte has incombustibility, high capacitance, as well as high power density when compared to EDLCs containing other electrolyte systems.\(^\text{1-3}\)

In regard to electrode active material for EDLCs, activated carbon has been used even in most aqueous EDLCs, because activated carbon has a large surface area and enough chemical stability.\(^\text{2,4}\) Generally, however, an activated carbon electrode shows a high resistance in an aqueous electrolyte because activated carbon has an insufficient affinity for an aqueous electrolyte. In addition, fluorinated polymer material typically acting as a binder for EDLC electrodes also has a poor affinity for aqueous electrolytes. There is, therefore, a considerable resistance at an electrode/electrolyte interface in an aqueous EDLC. Some researchers have applied surface treatment to electrodes in an attempt to enhance their affinity for an electrolyte and hence decrease the electrode/electrolyte interface resistance.\(^\text{5-9}\)

In this study, we optimize an electrode/electrolyte interface resistance for aqueous EDLC systems by applying a novel methodology: hybridization of a small amount of deoxyribose nucleic acid (DNA) derivatives with activated carbon. Since Watson et al.\(^\text{10}\) reported the structure of DNA, a great number of studies concerning DNA have ranged over not only biochemistry and medicine but also electrochemistry. For example, Nakashima et al.\(^\text{11}\) reported that DNA solubilizes single-walled carbon nanotubes in water. Other researchers reported on an electrochemical sensor with DNA\(^\text{12}\) as well as self-assembly of carbon nanotubes by DNA mediation.\(^\text{13,14}\) Their reports supported or utilized the affinity of DNA for carbon. This study utilizes such DNA-carbon interaction for aqueous EDLC electrodes to eliminate a resistance at an electrode/electrolyte interface.

2 Experimental

Activated carbon powder (BCP, supplied by Toyobo Co, BET specific surface area: 800 m\(^2\) g\(^-1\), particle size: \(\sim 5\) \(\mu\)m in average diameter) was used as active material for the present electrodes, where applied binder was polytetrafluoroethylene (PTFE, F-104 Daikin Industries). We loaded single-strand DNA (molecular weight: \(\sim 10^5\), sodium salt type from salmon testes) into electrodes by mixing 30 mg of activated carbon powder with 2.5 wt.% PTFE and 2.5 wt.% DNA, which was an optimized electrode composition; too much DNA led to a decrease in the mechanical strength of the electrode, and DNA less than 2.5 wt.% was found to be ineffective. Thereafter, the activated carbon/DNA composite was pressed on Ni gauze (Nilaco, 100mesh) as a current collector for most of the present electrodes; in the case of H\(_2\)SO\(_4\) electrolyte, we used Pt gauze (Nilaco, 100mesh) because it is resistant to a H\(_2\)SO\(_4\) electrolyte. The obtained composite electrodes had approximately 400 \(\mu\)m thickness and 1.20 cm in diameter. Activated carbon electrodes without DNA were also prepared for comparison; they were composed of 95 wt.% activated carbon and 5 wt.% PTFE.

To evaluate effects of various electrolytes on the behavior of electrode/electrolyte interface, we applied 30
wt.% HSO₄, 2.0 M NH₄BF₄, 3.5 M NaBr, 4.0 M NaCl, 2.0 M Na₂SO₄, and 7.0 M KOH aqueous electrolytes. These electrolytes ranged from being strong acidic to strong basic. Prior to EDLC cell assembly, a pair of electrodes and a piece of glass-fiber filter paper (GB-100R, Advantec) as a separator were immersed in the selected electrolytes for 3 hours under a reduced pressure. A two-electrode cell with a Teflon case was then fabricated with a pair of the composite electrodes and the separator. The EDLC performances were evaluated by charge-discharge cycling under constant current conditions (2.5-25 mA cm⁻²) using HJ1001-SM8 (Hokuto Denko). The cutoff voltages were 0.8 V for charging and 0 V for discharging. Before the charge-discharge tests, fifty formation cycles were carried out at a current density of 2.5 mA cm⁻², because the dry, as-prepared electrodes have a high electrode/electrolyte resistance. All the experiments were performed at a room temperature, 25°C.

3 Results and Discussion

Generally, two representative techniques have so far been employed for electrode preparation: a wet process from slurry and a dry process from mixture without any solvents. In the present study, we applied a dry process because a wet process was found to change intrinsic DNA structure; DNA was degraded in a thermal drying process (120°C) for removing a solvent such as N-methylpyrrolidone from slurry.

Figure 1 shows the capacitance ratio, in percentage, of an activated carbon electrode containing DNA to the corresponding electrode without DNA in various aqueous electrolytes. Data concerning the capacitance ratio in each electrolyte were extensively collected also at various current densities as shown in Fig. 1. At relatively low current densities, no obvious difference in the capacitance ratio among the tested electrolytes was observed; these ratios were around 100%. This suggests that the effect of DNA-loading to the electrode on its capacitance is almost negligible at a low cycling current, irrespective of the applied electrolytes.

The capacitance ratio of the presence to absence of DNA increased, however, with an increase in current density especially in simple, neutral salt electrolytes: 4.0 M NaCl and 3.5 M NaBr aqueous systems. In addition, a slight increase in the capacitance ratio, a positive addition effect of DNA, was observed with increasing current density in a mild acidic electrolyte, 2.0 M NH₄BF₄ as well as a weakly alkaline electrolyte, 2.0 M Na₂SO₄. In contrast, no increase in the capacitance ratio was observed in strongly acidic 30 wt.% H₂SO₄ as well as strongly basic 7.0 M KOH electrolytes. These results mean that the extreme conditions far from a neutral solution degrade DNA-loading effect. Table 1 summarizes the typical values of capacitance ratio of the DNA-composite to non-composite electrodes in the tested electrolytes at the representative current densities. At a high current density (25 mA cm⁻²), the addition effect of DNA on the capacitance enhancement was significant: 823% and 211% in the 3.5 M NaBr and 4.0 M NaCl electrolytes, respectively. In marked contrast to these electrolytes, no increase was observed in the capacitance of electrodes with DNA-loading in the 7.0 M KOH and 30 wt.% H₂SO₄ electrolytes. In addition, in the other electrolytes, 2.0 M Na₂SO₄ and 2.0 M NH₄BF₄, discharging itself was impossible at all at such a high current density due to a high internal resistance irrespective of the presence of DNA.

Table 1 Typical values of percentage capacitance ratio (%) of the DNA-composite to non-composite electrodes in the tested electrolytes at the representative current densities.

<table>
<thead>
<tr>
<th>Current density</th>
<th>KOH</th>
<th>Na₂SO₄</th>
<th>NaCl</th>
<th>NaBr</th>
<th>NH₄BF₄</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 mA cm⁻²</td>
<td>96.9</td>
<td>103.2</td>
<td>102.3</td>
<td>104.2</td>
<td>101.4</td>
<td>104.7</td>
</tr>
<tr>
<td>12.5 mA cm⁻²</td>
<td>96.4</td>
<td>110.2</td>
<td>122.2</td>
<td>159.8</td>
<td>107.3</td>
<td>101.8</td>
</tr>
<tr>
<td>25.0 mA cm⁻²</td>
<td>98.4</td>
<td>a</td>
<td>211.3</td>
<td>832.7</td>
<td>a</td>
<td>98.7</td>
</tr>
</tbody>
</table>

*Discharge of electrode was impossible due to a large IR drop.

EDLCs composed of the DNA-loading and non-composite electrodes with the various electrolytes. The discharge capacitances for the strongly acidic and basic electrolytes were higher than those for the other electrolytes in all current densities: 25-25 mA cm⁻². This is because proton or hydroxide in a high concentration can provide a high capacitance on the activated carbon surface. At a high current density of 25 mA cm⁻², no discharge capacitance was observed in 2.0 M NH₄BF₄ and 20 M Na₂SO₄ with a crucial IR drop. Nonetheless, capacitances were still obtained in the neutral salt electrolytes even at the high current density; especially, DNA-loading to the electrodes can effectively enhance their capacitance. These results suggest that, irrespective of the presence of DNA, the neutral salt electrolytes inherently have compatibility with the electrodes by an osmotic effect probably due to their low viscosity, and that DNA distributed inside the electrodes can reduce the internal impedance of the electrodes.

To elucidate the DNA-loading effect, “capacitance retention” is defined as follows: 100 × C (25 mA cm⁻²) / C₀ (2.5 mA cm⁻²), where C₀ and C are discharge capaci-
Table 2  Discharge capacitances (F g⁻¹) of EDLCs composed of the DNA-loading and non composite electrodes with the various electrolytes and current densities.

<table>
<thead>
<tr>
<th>Current density</th>
<th>Electrode</th>
<th>KOH</th>
<th>Na₂SO₃</th>
<th>NaCl</th>
<th>NaBr</th>
<th>NH₄BF₄</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 mA cm⁻²</td>
<td>DNA-loading</td>
<td>226.2</td>
<td>152.8</td>
<td>133.2</td>
<td>140.5</td>
<td>151.4</td>
<td>240.5</td>
</tr>
<tr>
<td></td>
<td>without DNA</td>
<td>233.4</td>
<td>148.0</td>
<td>130.2</td>
<td>134.9</td>
<td>156.3</td>
<td>229.9</td>
</tr>
<tr>
<td>12.5 mA cm⁻²</td>
<td>DNA-loading</td>
<td>213.5</td>
<td>133.9</td>
<td>130.8</td>
<td>131.6</td>
<td>111.2</td>
<td>213.8</td>
</tr>
<tr>
<td></td>
<td>without DNA</td>
<td>221.5</td>
<td>120.7</td>
<td>107.1</td>
<td>82.4</td>
<td>103.2</td>
<td>210.0</td>
</tr>
<tr>
<td>25.0 mA cm⁻²</td>
<td>DNA-loading</td>
<td>192.5</td>
<td>a</td>
<td>118.5</td>
<td>112.3</td>
<td>a</td>
<td>189.4</td>
</tr>
<tr>
<td></td>
<td>without DNA</td>
<td>195.6</td>
<td>a</td>
<td>56.1</td>
<td>13.6</td>
<td>a</td>
<td>191.8</td>
</tr>
</tbody>
</table>

*Discharge of electrode was impossible due to a large IR drop.

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References