Improvement of Specific Capacitance with Addition of Surfactants to an Aqueous Electrolyte

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The effect of the addition of surfactants to an aqueous electrolyte on discharge property of the capacitor was investigated. Dodecylbenzene sulphonate surfactant drastically improved the specific capacitance of electric double layer capacitor (EDLC) electrode. The addition of surfactants promoted the electrolyte to access the interior portion of micro pores. EDLC effective area was increased and subsequently specific capacitance was also increased. However, the specific capacitance depended on chemical structure and concentration of the surfactants added. The adsorbed surfactants interfered with mobility of ions. This is another factor for decreasing the specific capacitance.

Key Words: Porous Carbon Electrode, Capacitance, Surfactant, Wettability

1 Introduction
An electric double layer capacitor (EDLC) has been used as a electric power back up system in many electric products. Recently, it is used in various fields, such as hybrid vehicles and mobile telecommunication systems. It is greatly expected in near future that EDLC will be employed in many fields from the viewpoint of energy and environment. Therefore, the energy density of the EDLC should be improved to satisfy the demanded performance. Increasing the specific capacitance is an effective method to improve of the energy density of EDLC. The development of porous carbon electrode is one of the effective methods. Many investigations have been focused on the pore structure of the carbon.1,5) However, the pore or porous surface of the carbon electrode is hydrophobic.6) Especially, the electrolyte which has high dielectric constant is hard to penetrate into the micro pore. If the effective area of electric double layer is enlarged, the specific capacitance is improved. Consequently, the modification of the pore or porous surface of the carbon has been reported.7) On the contrary, it is expected that addition of a surfactant to the electrolyte helps the electrolyte penetration into the micro pore.8) In this study, various kinds of the surfactants were added to the aqueous electrolyte. The effect of addition of the surfactants on the discharge property of the capacitor was discussed.

2 Experimental

2.1 Materials
A porous carbon (BET specific surface area: 1050 m$^2$/g) was prepared from a phenol resin used as the EDLC electrode without modification. Sulfuric acid used was commercial and special grade. The following commercially available surfactants were used: sodium dodecylbenzene sulphonate (DBS-Na), sodium ethylbenzene sulphonate (EBS-Na), sodium lauryl sulfate (LS-Na), sodium oleate (OA-Na), benzyltrimethylammonium chloride (BTMAC), dodecyltrimethylammonium chloride (DTMAC) and glycerine.

2.2 Procedure
The porous carbon material was crushed to less than 1.05 × 10$^{-4}$ cm diameter, 0.1 g of the powder was mixed with ca. 1 ml of 30 wt% H$_2$SO$_4$ which contained the surfactant (0.1 ~1 mol/L). The mixture of the porous carbon powder and the electrolyte was kept for 1.8 × 10$^3$ s under low pressure (less than 10 mm Hg) to promote inversion of the electrolyte into the carbon pore. The time under low pressure was enough long was confirmed by preliminary experimentation with changing the inverse time.

The test capacitor cell was two electrode type. The slurry was kept between two spacers of poly ethylene sheet (thickness 0.1 mm) contacted Pt plate (collector) (diameter 18 mm) with copper wire. A plastic mesh sheet (thickness 0.1 mm) was inserted between poly ethylene spacers as a separator. The effective surface area of the single collector was 7.07 × 10$^{-2}$ cm$^2$. The test cell was charged from 0 to 0.9 V at a constant current of 0.5 mA (36 mA/m$^2$). After keeping the voltage was kept at 0.9 V for 30 min, the cell was discharged at a constant current of 0.1 mA (7.1 mA/m$^2$) until 0.9 V decrease to 0 V. This operation was repeated for 100 cycles at 30°C. The specific capacitance (F/g-electrode material was calculated from the slope of time vs. voltage curve between 0.45~0.54 V in the (discharge process (NAGANO/BTS2004).

3 Results and Discussion

3.1 Effect of surfactant addition to electrolyte on the specific capacitance
 Various concentration (0.1 ~1 mol/L) of each organic surfactant was added to 30 wt% sulfuric acid. The specific capacitance was affected by kinds of surfactant and its
Table 1  Surfactants used in the present work.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Surfactant</th>
<th>abbr.</th>
<th>Structure</th>
<th>Carbon number of alkyl chain</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
<td>Sodium dodecylbenzene sulphonate</td>
<td>DBS-Na</td>
<td></td>
<td>12</td>
<td>SO$_3^-$</td>
</tr>
<tr>
<td></td>
<td>Sodium ethylbenzene sulphonate</td>
<td>EBS-Na</td>
<td></td>
<td>2</td>
<td>SO$_3^-$</td>
</tr>
<tr>
<td></td>
<td>Sodium lauryl sulfate</td>
<td>LS-Na</td>
<td></td>
<td>12</td>
<td>SO$_3^-$</td>
</tr>
<tr>
<td></td>
<td>Sodium oleate</td>
<td>OA-Na</td>
<td></td>
<td>18</td>
<td>CO$_3^-$</td>
</tr>
<tr>
<td>Cation</td>
<td>Benzyltrimethylammonium chloride</td>
<td>BTMAC</td>
<td></td>
<td>0</td>
<td>N(CH$_3$)$_3^+$</td>
</tr>
<tr>
<td></td>
<td>Dodecytrimethylammonium chloride</td>
<td>DTMAC</td>
<td></td>
<td>12</td>
<td>N(CH$_3$)$_3^+$</td>
</tr>
<tr>
<td>Neutral</td>
<td>Glycerine</td>
<td>glycerin</td>
<td></td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

concentration. The effect of surfactant addition to electrolyte on the specific capacitance was summarized in Table 1. DBS-Na and DTMAC increased the specific capacitance. Especially, DBS-Na gave remarkable effect to improve the capacitance. However, the effect of surfactant didn’t show the clear tendency on length of alkyl carbon chain and charge (cationic, anionic, or neutral).

The effect of concentration of the surfactants on the capacitance was shown in Fig. 1. The capacitances shown in Fig. 1 were observed at the 20th cycle of charge and discharge process. The capacitance of DBS increased with increasing concentration up to 0.3 mol/L, but deceased with increasing concentration further. The capacitance of BTMAC and DTMAC also increased with increasing concentration (0.1 and 0.8 mol/L, respectively), but deceased with further increase in concentration more. The capacitance kept constant when glycerine was added to electrolyte even though its concentration increased. The capacitance decreased with increasing of the concentration of EBS and LS. These results suggest that surfactant effect depended on a kind of surfactant and its concentrations. The highest capacitance was observed when DBS was added to the electrolyte. Hereafter, we examined to clarify the effect of DBS addition on the capacitance.

The effect of DBS concentration on each capacitance of the cycle test was shown in Fig. 2. The original specific capacitance of the carbon electrode was about 40 F/g. The specific capacitance depended on the DBS concentration. The highest specific capacitance was almost 70 F/g when the concentration of DBS was 0.3 mol/L. The capacitance was almost constant at each DBS concentration. This results suggested that effect of DBS on the charge and discharge processes was steady.

The discharge curves measured at each cycle of 1st ~ 100th when DBS was added to electrolyte were shown in Fig. 3. The discharge time was proportional to the weight of carbon electrode. Here, discharge time was divided by the weight of the carbon electrode to cancel the effect of the amount of carbon used. The internal resistance was not observed even though DBS was added to electrolyte. The discharge curve was almost straight. This result suggested that the addition of surfactants was able to improve the performance of porous carbon for capacitor electrode.

The effect of addition of surfactant was summarized in Fig. 4. (a) The surface of carbon matrix is hydrophobic.

![Fig. 1](image1.png) **Fig. 1** The effect of concentration of the surfactants on the capacitance.

![Fig. 2](image2.png) **Fig. 2** The effect of DBS concentration on each capacitance of the test cycle.

![Fig. 3](image3.png) **Fig. 3** The discharge curves measured at each cycle of 1st ~ 100th when DBS was added to electrolyte.
An aqueous electrolyte can’t go into the micro pore of carbon electrode. So, the effective area of surface, where electric double layer forms is less than the real surface area of the porous carbon electrode. (b) When a surfactant is dissolved in an aqueous electrolyte, the wettability of the electrolyte increased. The electrolyte can penetrate into the deep portion of the micro pore. The effective area of EDL becomes greater than before the addition of the surfactant. The surfactant is adsorbed on the pore surface of carbon. When the adsorption of the surfactant is small, the ions can move smoothly with charge and discharge operations. Subsequently, the specific capacitance becomes larger with increase of surfactant concentration. (c) When the concentration of the surfactant increases, the adsorption amount of the surfactant is large. The surfactant molecule which adsorbs in the pore disturbs the mass transfer of ions with the charge and discharge operations. The specific capacitance becomes smaller when the concentration of the surfactant is high.

The effect of the surfactant on the specific capacitance is mainly caused by the wettability and adsorption characteristics of the surfactants to the porous carbons. Physical properties of the electrolyte, such as, surface tension and viscosity also may show the relation to the surfactant effect. These physical properties are measured for the bulk solution. We assume that the penetration of the electrolyte to the pore is controlled not only surface tension and viscosity of the electrolyte but also the physical and chemical properties of the carbon pore. The details on the effect of the penetration of the electrolyte to the pore will be discussed elsewhere.

4 Conclusion

The effect of addition of the surfactants on the discharge property and specific capacitance of the capacitor was discussed. It can be summarized as follows.

1) Dodcylbenzene sulphonate (DBS-Na) drastically improved the specific capacitance of electric double layer electrode.

2) Addition of surfactants to an aqueous electrolyte promotes that the electrolyte immerses into the inner part of micro pore. The effective area of electric double layer formed was enlarged. The specific capacitance was improved.

3) The surfactants were adsorbed in the carbon pore. It interfered with mobile of ions. The specific capacitance decreased. The addition of DBS-Na decreased the capacitance even though when the concentration was high.

References