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Influences of Residual Water in High Specific Surface Area Carbon on the Capacitor Performances in an Organic Electrolyte Solution

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ABSTRACT

Charge-discharge behavior of an electric double-layer capacitor consisting of conventional activated carbon electrodes with an organic electrolyte solution have been investigated as a function of the amount of residual water in the carbon. The water contents in the carbon powder were estimated by the titration of the released water in acetonitrile solvent by assuming adsorption-distribution equilibrium between the solid carbon and the organic solvent phases. The residual water in the carbon much influenced the capacitor performances, especially in the cycling with high-rate or high-voltage floating. The constant-current cycling at higher current rates decreased the specific capacitance and increased the internal resistance for the electrodes containing higher amounts of residual water. The degradation behavior was more significantly observed for the electrode containing more water when the charge-discharge cycling was accompanied by high-voltage floating.

1. Introduction

Utilization of electrochemical capacitors has recently become more important in wide application areas ranged from portable electronics to efficient energy-harvesting systems [1–3]. In most cases, achieving higher energy density (or higher specific energy) is a key issue for developing advanced capacitor devices. The energy density of the capacitor device, U [Wh m^{-3}], is directly proportional to the square of the operation voltage, as shown in equation (1),

$$U = 1/2\ CE^2 \quad (1)$$

where C and E are the capacitance density [F m^{-3}] and the operation voltage [V], respectively. Thus, increasing the operation voltage would be quite effective to realize higher energy density of the capacitor device. However, the increasing the operation voltage generally tends to decrease the life of the capacitor devices, especially for those using organic electrolyte systems.

At the present, nominal working voltage of commercially available electric double-layer capacitors (EDLCs) with organic electrolyte systems is limited to 2.3 - 2.7 V for a single cell. Higher voltage for charging than 3 V tends to deteriorate the cycle durability [4–6]. Impurities in the electrolyte solution can also influence the capacitor performances, especially for the cycle retention of the capacitance. Among them, influences of water content in the organic electrolyte have widely investigated on the capacitor performances [7–9]. Kötz, et al. reported the influences of the operation voltage on the cycle performances of the carbon-based electrodes in organic electrolyte solutions [10–14]. They also demonstrated the importance of the residual water content in the electrolyte solution that affects critically the capacitance retention with repeated cycles [15].

As the carbon materials generally used in EDLCs have high specific surface area (m^2 g^{-1}) and complexed pore structures, they usually contain impurities in their pore structures. Especially, residual water strongly adsorbed inside the micro-pore may affect the capacitor behavior in non-aqueous organic electrolyte systems. However, its influences on the capacitor performances are still unclear because it is rather difficult to determine quantitatively the content of water that exists in nano-structure of porous carbon material after proper thermal treatments. We have recently proposed a simple method that can estimate the water contents in carbon materials having high specific surface area [16]. According to the analysis, the conventional activated carbon

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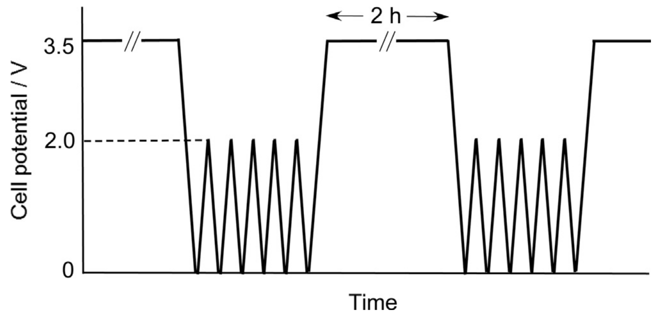

Fig. 1. Charge-discharge cycling mode including high-voltage floating for assessing the capacitor performance of AC-based electrodes.

(AC) contains some amounts of residual water even after thermal treatment with vacuum-drying. We also found that the level of the residual water can be controlled in some extent by choosing the drying conditions. In the present work, we have examined the cycle performances of AC electrodes containing different amounts of residual water. That is, AC samples containing different amounts of residual water were prepared by changing the drying conditions, and their capacitor performances were examined in an organic electrolyte solution. Influences of the trace level of water in the pore structure on the capacitance behavior were investigated in a conventional propylene carbonate (PC)-based solution using different charge-discharge cycling modes [17].

2. Experimental

Steam-activated high specific surface-area carbon (YP50F, Kuraray Chemical) was used as a test material. Samples containing different amounts of residual water were prepared by immersing the carbon material into deionized water under ambient temperature conditions followed by vacuum-drying (< 100 Pa) at 373 K for different hours. The amounts of residual water in the resulting carbon material were estimated from a water adsorption-distribution isotherm method, details of which are described elsewhere: The released amounts of water from carbon material to hydrophilic solvents, acetonitrile, were determined by Karl-Fisher titration as a function of the carbon/solvent mass ratio [16]. Here, the samples containing different amounts of residual water are

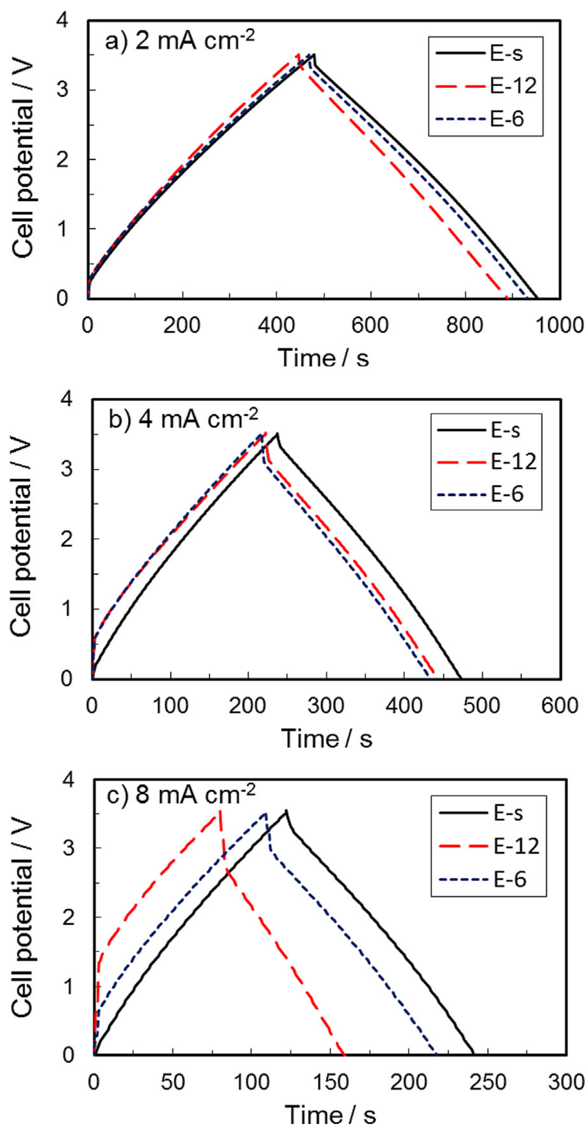

Fig. 2. Charge-discharge curves of AC-based electrodes containing different amounts of residual water at 100th cycle under constant current cycling.
a) 2 mA cm^{-2} (~0.35 A g^{-1}), b) 4 mA cm^{-2} (~0.70 A g^{-1}), c) 8 mA cm^{-2} (~1.4 A g^{-1}).

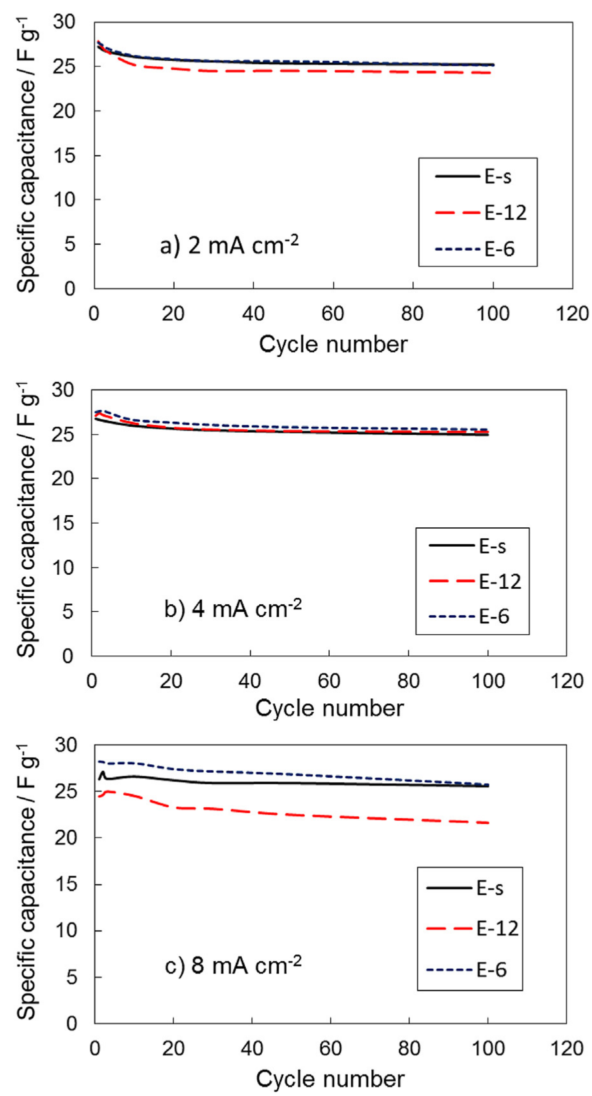

Fig. 3. Variations in the specific capacitance of AC-based electrodes containing different amounts of residual water in 1.0 M TEABF$_4$ with the charge-discharge cycling.
a) 2 mA cm^{-2} (~0.35 A g^{-1}), b) 4 mA cm^{-2} (~0.70 A g^{-1}), c) 8 mA cm^{-2} (~1.4 A g^{-1}).