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Competition between ionic adsorption and desorption on electrochemical double layer capacitor electrodes in acetonitrile solutions at different currents and temperatures

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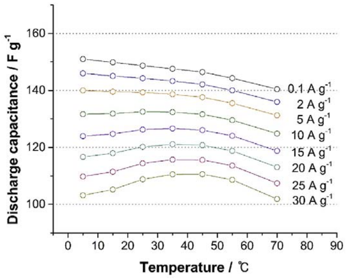
HIGHLIGHTS

- High-current operation leaves unoccupied sites on the electrode for ionic adsorption.
- Increasing the temperature stimulates ions to occupy the empty sites.
- Excessively high temperatures increase the desorption rate.
- The balance between adsorption and desorption peaks at mid-range temperatures.

GRAPHICAL ABSTRACT



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ABSTRACT

The operation of electrochemical double layer capacitors at high currents and viscosities and at low temperatures is difficult. Under these conditions, ion transport is limited, and some of the electrode area is unavailable for adsorption, which results in a low capacitance. Increasing the temperature helps to increase the ionic movement, leading to enhanced adsorption and increased capacitance. In contrast, ion desorption (self-discharge) surpasses the capacitance improvement when ions gain a high amount of energy with increasing temperature. For example, temperatures as high as 70 °C cause a very high rate of ionic desorption in acetonitrile solutions in which the individual properties of the two electrolytes—tetraethylammonium tetrafluoroborate (TEA BF_4) and ethylmethylimidazolium tetrafluoroborate (EMI BF_4)—are not distinguishable. The capacitance improvement and self-discharge are balanced, resulting in a capacitance peak at mid-range temperatures, i.e., 35–45 °C, in the more viscous electrolyte, i.e., TEA BF_4. The less viscous electrolyte, i.e., EMI BF_4 has a wider capacitance peak from 25 to 45 °C and higher capacitance than that of TEA BF_4. Because the maximum power is obtained in the mid-temperature range (35–45 °C), it is necessary to control the viscosity and temperature to obtain the maximum power in a given device.

1. Introduction

The rapid supply of energy and long cycle life of electrochemical double layer capacitors (EDLCs) allow frequent and persistent cell cycling, allowing their use in electric vehicles, such as electric buses [1] and trams [2], where quick charge facilities are available in every station. In addition, the fuel efficiency of vehicles can be improved by using regenerative brakes [3–6] and stop-start systems (or idle stop and go system) [7–9] by taking advantage of the rapid energy management of EDLCs. The operation of EDLCs at high currents causes the cell

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temperature to rise because of the cell resistance and reversible heat cycles [10]. In addition, in automobiles, the engine under the hood is another heat source that raises the cell temperature. Under these conditions, cells are constantly exposed to high and variable temperatures. While cells containing ionic liquids remain relatively stable at high temperatures [11–13], cells containing organic solvents suffer from increased vapor pressures at high temperatures [14]. These continual temperature changes have a negative effect on the cycle life of EDLCs because of the resultant electrochemical decomposition [15–17]. Nevertheless, if the temperature is well managed, the physical, chemical, and electrochemical damage can be limited; thus, it is necessary to find the optimum long-term operating conditions for a given device.

As the cell temperature increases, adsorbed ions on the EDLC electrode surface are desorbed, which reduces the coulombic efficiency of the cell. Even at room temperature, competition between ion adsorption and desorption exists. As soon as the charging process ends, the desorption of ions (self-discharge) becomes dominant. In this study, we investigated the change in behavior of energy-storage EDLCs with increasing temperature. The temperature dependence of the capacitance values at various currents can offer insights into the ion movement, adsorption, and desorption. Cell currents can change many factors for cells, for example, the operating time, ion population on the surface, and self-discharge time. Tetraethylammonium tetrafluoroborate (TEA BF_4) and ethylmethylimidazolium tetrafluoroborate (EMI BF_4) are the most widely used electrolyte salts for EDLCs. The individual properties of these two electrolytes [18] result in different cell behaviors. Understanding the adsorption and desorption behaviors, which are affected by many variables, can aid in the proper selection of cell operating conditions in terms of electrolytes, currents, and temperatures. In particular, we have studied the effect of temperature because long-term exposure to elevated temperatures can reduce the cycle life [19]. In addition, we focus on ionic adsorption and desorption behavior in cells where the electrolysis of the electrolytes over long cycles is not observed. The results from this study support further investigations into the severe electrolysis activities during long cycles.

2. Experimental

2.1. Materials

The syntheses of EMI BF_4 and TEA BF_4 have been reported elsewhere [18,20]. For the recrystallization of salts, all salts were dissolved in acetonitrile (AN, Sigma-Aldrich, 99.8%). *n*-Butanol was added to induce precipitation. The salts were filtered and dried thoroughly before use. The active material for the EDLC electrode was activated carbon (AC, CEP21KSN, Power Carbon Technology). The AC was mixed with an emulsion binder of styrene butyl rubber (SBR, Zeon, BM-400B), and carboxymethylcellulose (CMC, Sigma-Aldrich). Super-P black (MMM, Belgium) was used as the conducting agent. The active material, Super-P black, SBR, and CMC were mixed in a weight ratio of 81:12.8:4.2:2 to make a slurry. The slurry was spread on an Al foil and dried for 12 h at 80 °C under vacuum. The thickness of the prepared electrode was 150 μm. The electrodes were punched out into discs of 14-mm diameter and then dried in a vacuum oven. All salts were dissolved in AN, yielding 1.0 M electrolytes. Cell tests were performed using 2032-type coin cells (Hohsen Co.). Two carbon electrodes were used for the full cell tests. A 40-μm-thick cellulose separator was placed between the two electrodes, and the cells were assembled in a dry box.

2.2. Instruments

A cell test cycler (WBCS3000, WonATech Co., Ltd.) was used for the cell tests. Cell performances were evaluated using a galvanostatic charge and discharge procedure. The cell tests were performed by varying the temperature from 5 to 70 °C. The error range corresponding to each temperature value is listed in Table S2. Initially, the cells were charged to 2.7 V at a constant current. Then, the cells were discharged to 0 V. The discharge current was the same as the charge current. The cell capacitance was calculated from Eq. (1):

$$C = I/(\Delta V/\Delta t) \tag{1}$$

For the galvanostatic charge/discharge processes, the cell capacitance (F) was calculated from the current, I (A) and the denominator ($\Delta V/\Delta t$), which is obtained from the slope of the curve of voltage *vs.* time. The slope from 0 to 2.7 V was used to calculate the discharge capacitance from the galvanostatic tests. The capacitance values were averaged from three measurements. The specific capacitance (C_{am}) values of the electrodes (F g^{-1}) for all samples were obtained using Eq. (2).

$$C_{am} = 2C/m_{am} \tag{2}$$

Here, m_{am} is the mass of the active material (AC) in the electrode. In a symmetrical cell, the mass of each electrode is almost identical, and the value of m_{am} was obtained from the average mass of the AC used for the two electrodes in the cell.

Conductivity measurements were performed using a conductivity meter (Mettler Toledo, Seven Go Pro SG7-FK2) at the ambient temperature. A four-electrode conductivity probe (Mettler Toledo, Seven Go Pro Inlab 738) was calibrated with standards (Mettler Toledo) before the measurements were carried out. The viscosities of the electrolytes at room temperature were determined with a capillary viscometer (SI Analytics GmbH, 537 10) and a ViscoClock (SI Analytics GmbH). The reported viscosity of each electrolyte was averaged from five measurements. The conductivities and viscosities were measured in a dry box.

N_2 (99.999%) adsorption–desorption isotherms of the AC were obtained using a gas analyzer (MicrotracBEL Corp., BELSORP-max). Before analysis, the AC was outgassed at 300 °C for 4 h under a vacuum. The surface area was determined by the Brunauer–Emmett–Teller (BET) method. The total pore volume and surface area were obtained at relative pressures between 0 and 0.05 [21]. The surface area and pore size distributions for the AC used here are provided in Fig. S1 and Table S1 (Supporting Information). From the measurements, we found that 85.1% of the pores are micropores with pore diameters of < 2 nm.

3. Results and discussion

Curves of capacitance *vs.* current density for the electrodes in 1.0 M TEA BF_4 are shown in Fig. 1A; this figure shows the temperature dependence of the capacitance. The discharge capacitances at the lowest current density, 0.1 A g^{-1}, are higher than those at any other current densities because the low current allows sufficient time for ions to enter the narrow pores in the electrodes. At 0.1 A g^{-1}, the highest capacitance was obtained at the lowest temperature because the ion desorption rate is slower at low temperatures. The curves of voltage *vs.* time (Fig. 1B) were obtained from consecutive measurements between 5 and 70 °C at an operating current density of 0.1 A g^{-1}. The desorption rate increased with the temperature, as indicated by the shortening of the operation duration during discharge [11]. The accelerated desorption in the charge cycle is evidenced by the enlarging of the charge cut-off potential area (2.7 V), which is shown in Fig. 1C. Because the current density, 0.1 A g^{-1}, is very low, there is sufficient time for desorption to occur during both the charge and discharge processes. Fig. 1A shows the results as the current density was gradually increased to 30 A g^{-1}. From this figure, we found that elevated temperatures are advantageous for retaining the capacitance at high current densities. There is a cross-point (indicated by an arrow) in the capacitance values where the capacitance at higher temperatures is greater than that at lower temperatures. When the surface of an electrode is fully covered by adsorbed ions, the capacitance cannot be improved by changing the temperature. At high current densities, there is a very limited time for ions to travel into the pores. Therefore, many sites on the electrodes are unoccupied during high-current cycling. The higher temperature increases ionic