Cycle performance of lithium-ion capacitors using graphite negative electrodes at different pre-lithiation levels

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ABSTRACT

The specific capacitance of lithium-ion capacitors (LICs) in which the negative electrodes (NEs) of graphite were pre-lithiated at different levels was evaluated by cyclic charge–discharge tests. Two-electrode LIC cells operating at a working voltage of 2.2–3.8 V were assembled using a pre-lithiated graphite negative electrode (NE) and an activated carbon positive electrode (PE). It was shown that pre-lithiation of the graphite dictated the specific capacitance of LIC cells as well as their cycle performance. The increase in pre-lithiation level was responsible for the increase in specific capacitance and cycle stability. In the used LIC cells, high specific capacitance and the best cycle performance were accomplished at a pre-lithiation level of 71.1%, based on the theoretical Li intercalation capacity of graphite. Although higher pre-lithiation levels of 89.0% contributed to high specific capacitance in early cycling, they allowed a considerable decrease in specific capacitance at higher numbers of cycles. It was suggested that the Li intercalation capacity of the graphite NE provided by the pre-lithiation level and by cell charging should be designed not to exceed its theoretical capacity.

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1. Introduction

A lithium-ion capacitor (LIC) is an asymmetric electrochemical capacitor using a non-faradaic process of electrical double-layer formation on the positive electrode (PE) surface, as well as a faradaic process related to Li intercalation–deintercalation within the bulk of the negative electrode (NE). Five to ten times higher energy density than in conventional electrical double-layer capacitors (EDLCs) can be obtained from LICs with their existing benefits of high power density and long cycle life [1,2]. Therefore, LICs have wide potential applications, such as in renewable power generation systems, power backup systems, and energy recovery systems in industrial machinery.

Generally, LIC systems consist of an activated carbon PE, a separator, a carbon-based NE, and an electrolyte which is basically identical to those used in lithium-ion batteries (LIBs). One reason for using porous activated carbon for the PE is its high specific surface area to absorb and desorb a number of counterpart anions of Li^+, such as PF_6^-. Well-established materials for the NEs of LICs are graphite [3–8], amorphous carbon [9–11], and polyacene [12]. The effects of carbon types in the NEs on the electrochemical performance of LICs have been extensively investigated [13–16].

Among its notable features, graphite has a high theoretical capacity of 372 mAh/g and a low initial irreversible capacity of 5–20% [17]. Graphite in which Li is sufficiently doped shows a sufficiently low redox potential (<0.1 V *vs.* Li/Li$^+$) and a flat potential profile during Li intercalation–deintercalation [3]. This excellent property can alleviate electrolyte decomposition resulting from the increased redox potential (>4.5 V *vs.* Li/Li$^+$) at the PE [18,19].

The process of pre-lithiation or Li pre-doping is essential to provide graphite with a low redox potential, thus elevating the working voltage of the cell, which is typically 2.0–4.0 V. The potential swing at the graphite NE during Li intercalation–deintercalation can affect the capacitance and the cycle stability of the cells [19,20]. Zhang et al. have studied the effect of the degree of pre-lithiation of graphite-type NEs (mesocarbon microbeads, MCMBs) on the electrochemical performance of LICs [21]. In Zhang's work, the energy density of LICs using MCMB pre-lithiated at 0–94.1%, which was based on the theoretical Li intercalation capacity of graphite was evaluated by cyclic charge–discharge tests of 1000 cycles. Yuan et al. also evaluated the cycle and rate performance of LIC cells in which graphite NEs were pre-lithiated at different levels [2]. The cell containing a graphite NE pre-lithiated by short-circuiting for 8 h showed the best cycle performance. Although Yuan et al. did not clearly show the pre-lithiation level in the graphite provided by short-circuiting for 8 h, it was stated that there was an optimum Li pre-doping level to accomplish best cycle performance.

To achieve the full potential of graphite for use in the NEs of LICs and therefore, to improve cell performance, further pre-lithiation process optimization studies are needed. In the present study, the cycle performance of LIC cells with graphite NEs pre-lithiated at different levels was evaluated as a function of the number of cycles, under more severe conditions to accelerate the aging of the graphite NE. A spherulitic graphite pre-lithiated using a conventional lithium-ion battery (LIB) system was used for the NEs of the LIC cells. NEs and PEs aged by the cyclic test were carefully studied to understand the mechanisms of performance deterioration.

2. Experimental

2.1. Pre-lithiation of graphite

Graphite powder on a Cu foil current collector (HS-LIB-N-Gr-001, Hohsen Corp., Japan), which was intended for the NE of LIBs was used. The graphite layer was composed of spherulitic graphite, flake graphite at 14 mass%, and a binder of polyvinylidene difluoride (PVDF) at 7 mass%. The graphite layer with Cu foil was punched out into a disc (ϕ: 15 mm). The punched graphite layer, which was a mixture of spherulitic graphite, flake graphite, and PVDF was defined as the NE. The Cu foil current collector was not included in the NE. Mass and thickness of the NE were 9.0 mg and 36 μm, respectively. The NE was pre-lithiated using a LIB charge–discharge system consisting of $LiCoO_2$ coated on an Al foil current collector (ϕ: 15 mm), two pieces of cellulose-type separator (ϕ: 23 mm, thickness: 36 μm, TF4035, Nippon Kodoshi Corp., Japan), and the graphite NE with Cu foil, all of which were dried at 120 °C in vacuum and then sandwiched and sealed with 3 mL electrolyte in a two-electrode cell system made of SUS 304 steel (HS cell, Hohsen Corp., Japan). The electrolyte in use was a mixture of ethylene carbonate/diethyl carbonate (1:1 by vol.) containing 1 mol/L $LiPF_6$ (Kishida Chemical Co., Ltd., Japan). This LIB cell was assembled in an Ar-filled glove box. Different pre-lithiation voltages were applied across the graphite NE and the $LiCoO_2$. Using battery charge–discharge equipment (HJ1005SD8, Hokuto Denko Corp., Japan), the LIB cell was charged at a constant current of 2.5 mA (278 mA/g-NE). Once the cell voltage had reached the specified pre-lithiation voltage, it was held for 2 h with fading current. The charge–discharge processes for pre-lithiation were carried out at 25 °C.

2.2. Assembly of LIC cells

Commercial microporous AC powder (AP15, AT Electrode Co., Ltd., Japan), which can be used as EDLC electrodes was used for the PE of the LIC cells. The Brunauer–Emmett–Teller (BET) specific surface area of this AC was measured as 1454 m^2/g based on nitrogen adsorption–desorption isotherms obtained by a gas adsorption analyzer (Autosorb-iQ, Quantachrome Instruments Inc., USA). A mixture of the AC, a conductive agent of acetylene black (Denka Black, Denki Kagaku Kogyo, Japan) at 10 mass%, and a polytetrafluoroethylene binder (Polyflon D210-C, Daikin Industries Ltd.) at 10 mass% was ground with addition of ethanol. The mixture was pressed and molded into a thin sheet. The sheet was dried in air at 100 °C for >6 h and was then punched out into a disc. The disc was dried at 140 °C in vacuum. The disc (ϕ: 12 mm, thickness: 0.38 mm, mass: 24 mg) was used as the PE of the LIC cells and was attached to an Al mesh current collector (ϕ: 15 mm). The Al mesh current collector was not included as part of the PE.

The LIB cell containing the pre-lithiated graphite NE was opened, and the $LiCoO_2$ was replaced by the AC PE with Al mesh in an Ar-filled dried glove box. The LIC cell was sealed again and was subjected to a cyclic charge–discharge test. Fig. 1 shows scanning
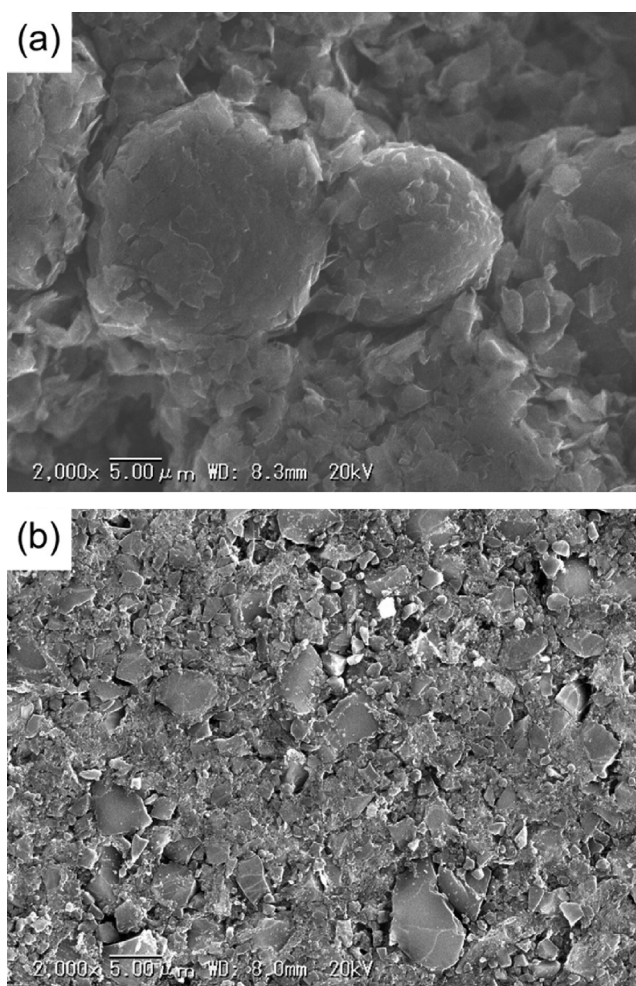

Fig. 1. Scanning electron micrographs of the graphite NE and the AC PE used for LIC cells. (a) graphite NE, (b) AC PE.

electron micrographs of the graphite used for the NE and the AC used for the PE. The mass ratio of PE to NE in the LIC cell was 2.7. Fig. 2 shows the experimental setups for pre-lithiation, cell assembly, and the charge–discharge test.

2.3. Cyclic charge–discharge test

The voltage and current values and their relationship to LIC cell performance are shown in Fig. 3. *V* and *I* are the time-varying cell voltage and current, respectively. The units of *I* are mA/g-PE&NE, which means the actual charge or discharge current divided by the sum of the PE and NE masses. I_C and I_D, with units of mA/g-PE&NE, indicate the constant current density for the charge and discharge processes, respectively. Here, I_C was set to –73 mA/g-PE&NE, and I_D was set to +73 mA/g-PE&NE. The current flow direction during the discharge was defined to be positive. V_H and V_L (both *V*) are the high and low cutoff voltages, respectively, and set to 3.8 and 2.2 V. V_{IR} is the voltage IR drop at the start of the discharge process. T_H is the voltage-holding duration in both the charge and discharge stages and was determined to 0.5 h. One charge–discharge cycle included the charge period in which the voltage increased from 2.2 to 3.8 V at 73 mA/g-PE&NE and was maintained at 3.8 V for 0.5 h, as well as the discharge period in which the voltage decreased at 73 mA/g-PE&NE and was maintained at 2.2 V for 0.5 h. The charge–discharge cycle was repeated 100 times.

The specific capacitance of the LIC cell, *C* (F/g-PE&NE) was calculated using Eq. (1):