



Incorporation of conductive polymer into soft carbon electrodes for lithium ion capacitors



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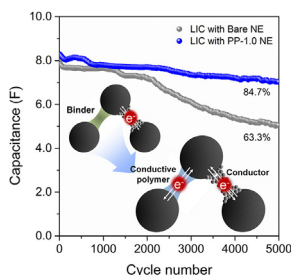
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HIGHLIGHTS

- Incorporation of conductive PEDOT-PSS allows a faster Li⁺ insertion into soft carbon.
- The soft carbon with 1.0 wt% PEDOT-PSS exhibits a capacity retention of 64% at 5 C.
- The LIC with 1.0 wt% PEDOT-PSS retains 85% of initial capacitance after 5000 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

The positive effects of incorporating electrically conductive poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT-PSS) into the negative electrode (NE) of a lithium ion capacitor (LIC) is investigated. The binding material of the NE, styrene-butadiene rubber (SBR), is partially substituted by conductive PEDOT-PSS. The soft carbon NE with 1.0 wt% PEDOT-PSS exhibits enhanced capacity retention of 64% at a current density of 5 C by lowering its electrical and electrochemical charge transfer resistance. The rate capability increased with increasing amounts of PEDOT-PSS, with no variation in the Li⁺ diffusivity. This improved electrochemical performance of the NE is also reflected in the LIC full-cell configuration. An LIC employing a 1.0 wt% PEDOT-PSS NE delivers 6.6 F at a high current density of 100 C, which is higher than the 6.0 F measured for the LIC with a bare NE. Moreover, the LIC with the 1.0 wt% PEDOT-PSS NE retains 85% of its initial capacitance even after 5000 cycles. These results are mainly attributed to the favourable electrical network formed by the incorporation of PEDOT-PSS into the NE. Thus, we believe that the incorporation of conductive PEDOT-PSS is a viable approach for obtaining high-power LICs.

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1. Introduction

Electrochemical double-layer capacitors (EDLCs) are the most promising energy storage devices for power quality applications in

portable electronics, electric transportation, and renewable energy generation [1–4]. Although EDLCs that offer high power capability and excellent cycle life have already been commercialized, their energy density is still limited as compared with rechargeable batteries [5–7]. There is therefore keen interest in further increasing the energy density of EDLCs for extending their application to transportation or stationary energy storage. A number of hybrid capacitors have been proposed with this goal in mind, with asymmetric cell configurations that allow for improved energy density [8–11]. Lithium ion capacitors (LICs), known as promising hybrid capacitors, have also attracted much attention because they can provide approximately three times higher energy density than conventional EDLCs [8,12–16].

LICs are composed of activated carbon as a positive electrode (PE) and Li^+ -inserting materials (e.g. graphite, hard carbon, soft carbon, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) as a negative electrode (NE). In contrast to the symmetric electrochemical behaviour of EDLCs, LICs show asymmetric charge–discharge profiles that combine a non-Faradaic reaction (adsorption/desorption of anions) in the PE and a Faradaic reaction (insertion/extraction of Li^+) in the NE close to 0 V vs. Li/Li^+ . This enables a higher operating voltage up to ~4.2 V, which is much higher than that of conventional EDLCs (~3.0 V). In this hybrid configuration, however, the power capability and cycle performance of LICs are strongly dependent on the material characteristics of the NE because the Li^+ insertion/extraction in the NE is much slower than its counter reaction in the PE. Among the various NE materials, graphite is considered a promising candidate as it allows the most extended operating voltage of LICs owing to its low and flat redox potential of approximately 0 V vs. Li/Li^+ . However, graphite suffers from its poor rate capability and cycle performance arising from the sluggish kinetics of Li^+ mobility in the highly ordered crystal structure. In contrast, as proposed by Amattucci et al. [8] $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows great promise as a suitable NE material for LICs because of its excellent rate capability and cycle performance [17–19], but the high redox potential of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ of approximately 1.5 V vs. Li/Li^+ limits the practical operating voltage of LICs (1.0–3.2 V).

On the other hand, soft carbon is a suitable choice for ensuring not only good rate capability and cycle performance but also a relatively extended operating voltage for LICs. In practice, soft carbon has numerous intercalation channels of Li^+ , good structural stability, and a low reaction voltage profile owing to its low crystallinity, characteristics that are mainly responsible for the good rate capability and cycle performance [20,21]. Despite such advantages, it is crucial to enhance the Li^+ insertion and extraction characteristics of soft carbon for further improvement of current LICs. One possible approach is to incorporate electrical conductive polymers such as polyaniline, polyacetylene, polypyrrole, and polythiophene into the NE. As confirmed by many studies, conductive polymers can effectively improve the electrode performance of batteries or capacitors [22–25] by utilizing additional electric conduction pathways and minimizing charge transfer resistance during cycling.

Herein, we propose incorporating poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT-PSS) into a soft carbon electrode as the NE, and we demonstrate the improved electrochemical performance of the NE for practical use in LICs. The incorporation of PEDOT-PSS enhances the electrical conductivity of the NE and, by extension, the electrochemical performance of the LIC because it is highly conductive, mechanically durable, stable in the oxidized state, and insoluble in common carbonate solvents (e.g. electrolytes). Accordingly, partial substitution of a conventional polymer binder with the conductive PEDOT-PSS in the NE allows the formation of an additional electrical network between the active material particles. It is essential for improving the rate

capability of the NE without cyclic performance fading. The results show that in comparison with a bare soft carbon NE, incorporating PEDOT-PSS improves the electrochemical performances of LICs.

2. Experimental

2.1. Preparation of electrodes

The bare NE was prepared with a slurry containing 90 wt% soft carbon (GS Energy Co., Korea), 5 wt% conducting carbon (Super-P, TIMCAL Co.), 2.5 wt% carboxymethyl cellulose (CMC), and 2.5 wt% styrene-butadiene rubber (SBR) in distilled water. Meanwhile, the SBR was partially substituted with 0.5 wt% and 1.0 wt% PEDOT-PSS (Sigma–Aldrich Co.) for preparation of the NEs, which were denoted as PP-0.5 NE and PP-1.0 NE, respectively. The slurries were applied to a mesh-type Cu current collector using vertical coating equipment and the loading amount was fixed at 6.5 mg cm^{-2} for each NE. The NEs were dried in a convection oven and roll-pressed up to density of 0.6 g cm^{-3} . The PE was prepared following the same procedure as the NEs using Al mesh with 80 wt% activated carbon (MSP-20, Kansai Coke and Chemicals Co.), 10 wt% conducting carbon (Super-P), and 10 wt% PVdF (polyvinylidene fluoride, Sigma–Aldrich Co.). The PE had a loading amount of 5.2 mg cm^{-2} and a density of 0.5 g cm^{-3} . The detailed specifications of the soft carbon NEs are provided in Table S2. The PEDOT-PSS incorporation into the NEs was confirmed by Fourier transform infrared spectroscopy (FT-IR, PerkinElmer Co.) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific Co.). The electrical conductivity of the as-prepared NEs was measured by the four-point probe method.

2.2. Electrochemical measurements

Half-cell test – CR2032 coin-type half-cells were assembled in a dry room by stacking a working electrode, a separator (polyethylene, Asahi Co.), and a metallic Li counter electrode. These components were immersed together in an electrolyte consisting of 1.3 M LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC, 3:7 volume ratio, PANAX E-tec Co.). The rate capability was examined in the voltage range of 0.01–1.5 V (vs. Li/Li^+) at current densities from 0.2 C (50 mA g^{-1}) to 5 C (1250 mA g^{-1}) using a battery tester (MACCOR series 4000). For the electrochemical impedance spectroscopy (EIS) measurements, a metallic Li reference electrode was added to the above mentioned half-cell configuration and the cells were evaluated within the frequency range of 1.0 MHz–10 mHz.

Full-cell test – Pouch-type LIC full cells $34 \times 50 \text{ mm}$ in size were assembled in a dry room using the same electrolyte and separator as for the half cell. Li^+ pre-doping into the NE, an essential lithiation process for proper operation of LICs, was carried out using an auxiliary Li metal electrode under a constant voltage of 0.01 V (vs. Li/Li^+) and the doping level was carefully controlled to be 80% of the practical capacity of the soft carbon NE (250 mAh g^{-1}). The LICs were galvanostatically charged and discharged at current densities from 0.2 C (17 mA g^{-1}) to 200 C (17 A g^{-1}) in the voltage range of 1.5–3.9 V. The cycling performance was tested with a constant current of 10 C (850 mA g^{-1}) over 5000 cycles, and EIS was performed under the same conditions as for the half-cell.

3. Results and discussion

The PP-0.5 and PP-1.0 NEs were prepared by partial substitution of SBR binder with 0.5 and 1.0 wt% of conductive PEDOT-PSS polymer, respectively, to investigate the effects of PEDOT-PSS incorporation on the electrochemical performance of soft carbon NEs. Unlike the insulating SBR binder, it is expected that PEDOT-PSS

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