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A Fast and Efficient Pre-doping Approach to High Energy Density Lithium-Ion Hybrid Capacitors

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Abstract: We demonstrate that the internal short (IS) approach is a fast and efficient process for the lithium pre-doping in the lithium-ion capacitors. Direct contact between graphite electrode and lithium metal leads to very fast but controllable lithium pre-doping into the graphite due to the large contacting
10 area in the excess electrolyte medium facilitated not only fast lithium interaction into graphite but also fast dissipation of reaction heat generated during this lithium intercalation process. The LIC cells pre-doped through IS method exhibit remarkably higher coulombic efficiency and longer cycle life than the cells prepared with conventional pre-doping methods such as electrochemical (EC) and external short circuit (ESC) methods. These results indicates that the IS pre-doping approach can significantly improve
15 the anode manufacturing speed and reduce the cost of the high energy density lithium-ion capacitors.

Introduction

Supercapacitors are promising energy storage devices due to their higher energy density than dielectric capacitors and higher
20 power density and long cycle life time compared with conventional batteries.[1-4] In order to meet the demands of a wide range of energy technologies such as hybrid electric vehicles, backup power sources and portable electronic equipment, supercapacitors with higher energy (and power) densities are
25 required.[1, 5-9] In the past decade a large number of ideas have sought to improve upon state-of-art supercapacitors.[1, 4-13] Due to their high energy density (more than three times higher than that of the electric double-layer capacitors (EDLC)), high power density and long cycle-life comparable to EDLC,[1, 4, 12-25] lithium-
30 ion capacitors (LIC) have recently received considerable attentions as advanced electrochemical energy storage devices[26-37]. In the LICs, a lithium intercalating anode of lithium-ion battery (LIB) and an activated carbon (AC) cathode of EDLC are asymmetrically combined, as illustrated in Figure 1a. During
35 charging and discharging of LICs, adsorption and desorption of anions occur on the AC cathode via non-faradic process, whereas intercalation and de-intercalation of Li^+ ions takes place on the anode through faradic process. Earlier studies have shown that lithium pre-doping in carbonaceous material anode such as
40 graphite is critical in achieving high energy density and long cycle life of LICs, because lithium doped graphite anode is capable of keeping the anode potential voltage as low as that of lithium metal and achieving large operation voltage in the cell, as shown in Figure 1b.
45 Lithium pre-doping provides preliminary lithium-intercalation into the graphite anode using an auxiliary lithium metal electrode before charging of AC/Graphite LIC full-cell. In general, the

lithium pre-doping of graphite anode is carried out using either electrochemical (EC) or external short circuit (ESC) methods
50 with a sacrificial lithium metal electrode as a lithium-ion source in non-aqueous electrolyte,[35, 36] as illustrated in Figure 1c. The two electrodes are separated by a porous polyolefin separator in nonaqueous electrolyte. However, EC and ESC processes require very long pre-doping time (> 10 h) to reach the sufficient and
55 uniform lithium pre-doping level, which increase the cost of the high energy density lithium-ion capacitors.
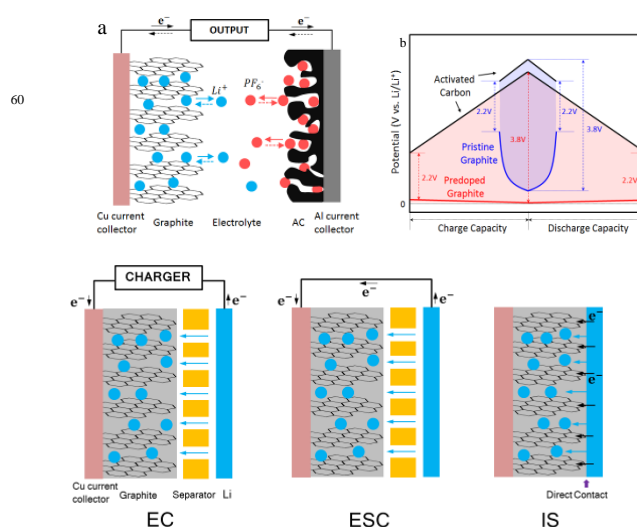

Figure 1. a) Schematic diagrams of LIC full-cell composed of activated carbon cathode and pre-doped graphite anode. b) Typical charge-discharge profiles of the AC/graphite cells with pristine graphite (blue line) and lithium-pre-doped graphite (red line) electrodes. c) Schematic

diagrams of three different pre-doping methods: EC, ESC and IS.

Here, we introduce a fast and effective approach to pre-dope the anode of lithium-ion capacitors by exploiting internal short (IS) for the LICs. As demonstrated in this paper, the IS can increase the pre-doping speed to 400% higher in comparison to the conventional ES and ESC doping processes. The AC/Graphite LIC full-cell prepared through the IS process has significantly better coulombic efficiency and longer cycle life than those fabricated from the conventional methods. No safety issue, including exothermic explosive behavior, rapid temperature rise and electrolyte degradation was found during IS pre-doping. The advantages of IS are attributed to the large electrochemical potential difference and to the direct contact over the wide area between graphite and lithium electrodes in a non-aqueous electrolyte, as illustrated in Figure 1c.

Besides the IS pre-doping approach, the traditional ES and ESC approaches were also investigated for the comparison. The EC pre-doping was performed using an electronic charger with an option of constant cut-off voltage (0.05 V vs. Li/Li$^+$). In the ESC pre-doping method, graphite electrode and sacrificial lithium metal electrode were separated with porous polyolefin separator in the electrolyte, and externally connected each other with an electric cable. In contrast, in the IS pre-doping method, graphite electrode was directly in contact with lithium metal electrode in electrolyte (see Supporting video clip) and there was no need of electronic charger or external electric circuit. During IS pre-doping, any safety concern, including exothermic explosive behavior, rapid temperature rise, and electrolyte degradation did not appear.

Experimental

Materials

AC electrode (ECE-162D) with aluminum current collector was purchased as mass-producing grade for EDLC from Korea JCC Co., South Korea. The AC electrode, consisting of 90 wt% AC, 5 wt% super P and 5 wt% binder, had a thickness of 68 μm. Graphite electrode with copper current collector, consisting of 90 wt% graphite and 10 wt% binder, had a thickness of 65 μm. The specific surface area of AC was 1,057 m^2/g. Lithium metal was purchased from Honjo Metal Co., Japan. Porous polyolefin separator (Celgard 2320 Trilayer, USA) with a thickness of 20 μm was used as separator. The battery-grade electrolyte, 1.0 M LiPF6 in ethylene carbonate/diethyl carbonate (3/7, v/v) was received from Soulbrain Co., South Korea, and used without further purification.

Fabrication of graphite/Li half-cell for pre-doping and de-doping

All the pre-doping and de-doping tests were in the home-made graphite/Li pouch cell with graphite electrode (32 mm × 25 mm) and lithium metal (40 mm × 30 mm). For EC and ESC pre-doping methods, a porous polyolefin separator (Celgard 2320) was placed between two electrodes and the electrolyte was filled to a predetermined weight (0.65 g). EC pre-doping tests were carried out using battery cycler (WBCS3000, WonATech Co., South Korea) in constant voltage mode (50mV, 4~60 min cut off). In the case of ESC pre-doping test, graphite electrode and

lithium metal electrode were externally connected using an electric wire to establish external short circuit. For IS pre-doping, graphite electrode was directly contacted to the lithium metal sheet without a separator in the electrolyte. After pre-doping, lithium metal in IS pre-doping cell was replaced with a new lithium metal, which was covered with a separator for de-doping test. The graphite/Li pouch cells during pre-doping and de-doping were compressed with two acryl plates to minimize the bulk resistance. All the fabrication processes were finished in an argon filled glove box.

Fabrication of lithium-ion capacitor (LIC) full-cell

For the charge and discharge measurements of LIC full-cells, Graphite (32 mm ×27 mm)/Li (34 mm × 28 mm)/AC (30 mm × 25 mm) configuration was used. First, graphite/Li unit was used to pre-dope graphite electrode, then lithium metal was removed to measure charge/discharge test of lithium doped-graphite/AC full-cell.

Characterizations

The EC pre-doping tests were carried out using battery cycler (WBCS3000, WonATech Co., South Korea) in constant voltage mode (50 mV, 4 ~ 60 min cut off). All de-doping tests were carried out using battery cycler on constant current mode (0.03 C, 3.0 V vs. Li/Li$^+$ cut off). Charge and discharge tests of LIC full-cells were carried out using battery cycler. Capacitors were charged with constant current (0.2 C) from their open circuit voltage (OCV) to 3.8 V (vs Li/Li$^+$), and discharged to 2.2 V to confirm the low rate charge/discharge performances.
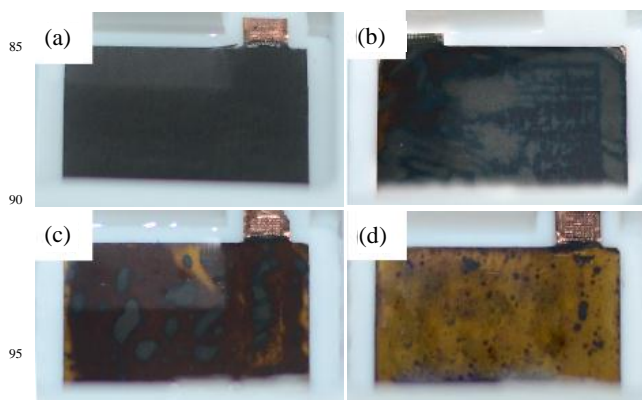
Results and Discussion

Figure 2. Photographs of graphite electrodes before (a) and after being pre-doped via EC (b), ESC (c), and IS (d) methods at constant doping time of 30 min.

Figure 2 compares the graphite electrodes before and after being pre-doped via three different methods at constant doping time of 30 min. The figure shows that the pristine graphite electrode has black color (Figure 2a), the EC pre-doped graphite electrode was dark brown in color (Figure 2b), ESC pre-doped graphite electrode was yellowish brown (Figure 2c), and the graphite electrode with IS has strong golden color as shown in Figure 2d. Generally, the color of graphite electrode depends on the degree of lithium pre-doping[38-42]. As the degree of pre-doping

increased, the color of graphite electrode changed from black to golden color, as shown in Figure S1. This clearly demonstrates that IS can provide higher lithium pre-doping content than EC and ESC for the same doping time.
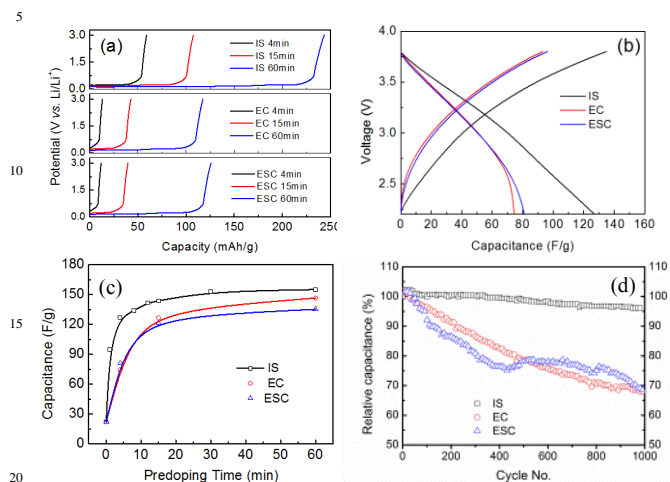

Figure 3. (a) 0.03 C Discharge curves of graphite electrodes pre-doped via EC, ESC and IS methods, (b) 0.2 C Charge-discharge curves of graphite electrodes pre-doped through EC, ESC and IS method, and (c) 0.2 C Discharge capacitances of LIC full-cells with different pre-doping methods as a function of pre-doping time and (d) 10.0 C Cycle life of the LIC full-cells.

Lithium pre-doping content is further evaluated quantitatively using discharge profiles of the graphite electrodes. Figure 3a shows the discharge profiles of the graphite electrodes pre-doped with three different methods at various doping times. The de-doping tests were conducted using a half-cell consisting of the pre-doped graphite anode and lithium metal electrodes at a very slow discharge rate of 0.03 C to minimize the resistance factors. Initial potential of the pre-doped graphite electrode depends on the degree of lithium pre-doping. During the de-doping process, the value of potential for the pre-doped graphite remained small up to a certain point and then abruptly increased to the potential of pristine graphite (3.3 V vs. Li/Li$^+$). The sharp potential increase is attributed to the shortage of lithium intercalated in the graphite electrode, because the graphite potential value is influenced by the degree of lithium pre-doping, as shown in Figure S2. The de-doping capacity depends critically on the pre-doping method. The IS pre-doped graphite electrodes with 4, 15, and 60 min doping time achieved capacity values of 60, 108, and 244 mAh g^{-1}, respectively. In contrast, the EC pre-doped electrodes in 4, 15, and 60 min exhibit the smallest discharge capacities of 13, 42, and 117 mAh g^{-1}, respectively. The ESC pre-doped electrodes for 4, 15, and 60 min have capacity values of 11, 39, and 125 mAh g^{-1}, respectively. These results demonstrate that the IS pre-doping provides much faster lithium pre-doping kinetics than the conventional EC and ESC pre-doping methods, and the graphite anode pre-doped by IS has capacity 100%-400% higher than the anodes prepared by the EC or ESC methods.

Figure 3b presents charge-discharge profiles of AC/graphite LIC full-cells. The capacitances were measured at the current rate of 0.2 C and voltage range of 2.2–3.8 V. Each graphite anode was pre-doped for 4 min via three different methods. The AC electrode used here had a capacitance of 160 F g^{-1} in the Li/AC half-cell test at the same voltage window (Figure S3). The cell

with the IS pre-doped graphite anode exhibited linear potential decrease without any sudden voltage drop. The IS cell delivered 134 F g^{-1} charge capacitance and 127 F g^{-1} discharge capacitance. In contrast, the full-cell with EC pre-doped graphite anode has 93 F g^{-1} charge capacitance and 74 F g^{-1} discharge capacitance. During the discharge test, the potential decreased sharply at 2.7 V. The cell with ESC pre-doped graphite electrode showed similar charge-discharge profile as the EC pre-doped graphite. The sudden voltage drops of EC and ESC cells are attributed to the shortage of lithium-ion source for adsorption onto the AC electrode, and potential shift of graphite electrode to positive direction due to shortage of the lithium intercalated into the graphite.[31, 35-37, 43] Both are essentially caused by the shortage of lithium intercalated in the graphite electrode. It indicates that IS pre-doping intercalated sufficient lithium into the graphite electrode within 4 min, while the EC and ESC pre-doping requires much longer time to reach that. Moreover, the shortage of intercalated lithium in EC and ESC methods leads to a poor coulombic efficiency of less than 80%, while IS produces the highest coulombic efficiency of 95%.

Figure 3c shows discharge capacitance values of AC/graphite full-cells prepared through three pre-doping methods at various pre-doping times. The EC and ESC cells exhibited similar trend of capacitance increase with pre-doping time. After 4 min doping, the EC and ESC cells have capacitance values of 74 and 80 F g^{-1}, respectively. In contrast, IS showed much faster capacitance increase with doping time than EC and ESC. The capacitance value reached almost saturation point of 127 F g^{-1} after 4 min and then slowly increases with the doping time.

Figure 3d shows the cycle life test results of AC/graphite full-cells with the graphite electrodes pre-doped via three different pre-doping methods. The 4 min IS cell showed capacitance retention of 96 % at the same conditions, while the capacitance of the 4 min EC and ESC cells reduces to 67% after 1000 cycles at 10 C. It is clear that IS cell provides not only larger capacitance but also much better cycle life than EC and ESC cells.
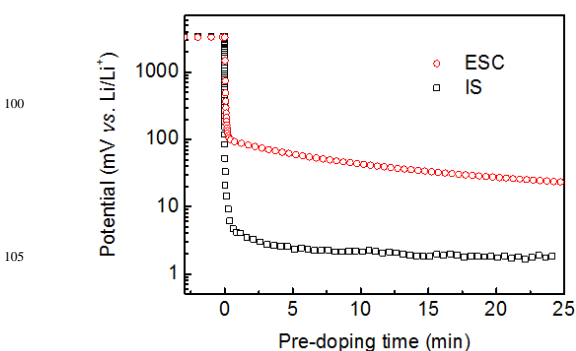

Figure 4. Potential profiles between graphite and lithium metal electrodes during the IS and EC pre-doping.

Figure 4 presents the electrochemical potential profile of graphite electrode against lithium electrode during pre-doping for the ESC and IS approaches. Potential profile during EC could not be observed because of the constant voltage mode for EC pre-doping. The potential was measured using a 3-electrode system consisting of an additional lithium metal as a reference electrode. For the IS pre-doping, initial potential of pristine graphite before

contacting to lithium electrode was 3.3 V vs. Li/Li⁺. As soon as both electrodes contacted, the potential of graphite electrode rapidly changed to 4 mV vs. Li/Li⁺ within 1 min and then slowly decreased nearly to the lithium metal potential with doping time. However, the potential did not reach 0.0 V, the lithium potential, even after sufficient time. During ESC pre-doping, potential changed to 100 mV within 1 min and then lowered to the lithium potential very slowly with doping time. That is, IS pre-doping process can provide smaller potential difference between graphite electrode and lithium reference electrode than ESC for the same doping time. It clearly indicates that IS method provides much faster pre-doping rate than ESC method.

Fundamentally, lithium pre-doping into the graphite electrode is driven by the potential difference between graphite electrode and lithium metal. In the cases of EC and ESC pre-doping methods, graphite and lithium were separated with a polyolefin separator with the thickness of 20 μm in non-aqueous electrolyte and the potential difference between two electrodes was 3.3 V. Because of this large electrochemical potential difference, lithium pre-doping into the graphite spontaneously takes place. Moreover, EC and ESC methods had the same ions transporting distance due to the presence of polyolefin separator between two electrodes; therefore, EC and ESC methods have almost the same pre-doping kinetics.

The pre-doping rate is also significantly influenced by diffusion rate of lithium-ion in electrolyte.[44-46] The lithium-ion diffusion rate is reciprocal to the distance between lithium metal and graphite electrodes.[47] During the IS pre-doping, lithium-ion have very short travel distance (almost zero gap) because of direct contact between lithium metal and graphite electrodes. Thus, IS method can provide much faster pre-doping rate than EC and ESC. Such distance effect on the pre-doping kinetics was also clearly observed in Li/graphite (EC pre-doped) with different separator thickness, as shown in Figure S4. The EC pre-doped graphite cell with a single layer separator showed two times faster pre-doping rate than that with double layer separator.

The IS process can provide very fast but controllable lithium pre-doping into the graphite electrode without any safety issues, such as abrupt temperature rise, extra decomposition of electrolyte, or explosive exothermic reaction. Interestingly, IS process did not form a regular close-loop electrical circuit but just had the direct contact between graphite and lithium metal electrodes. Nevertheless, IS method can achieve controllable lithium intercalation into the graphite electrode and electron transfer from lithium metal to graphite electrode, similar to those observed for EC and ESC. The stable electrochemical lithium intercalation in the IS was attributed to the resistive property of graphite layer (around 30 Ω in dry state). The graphite electrode consisted of graphite layer and Cu current collector. The resistive graphite layer could act as a buffer layer like an electronic resistor in the electrical circuit in the IS pre-doping and might play a key role in maintaining the potential difference between graphite and lithium metal even under the direct contact, as shown in Figure 4.

We note that the conventional internal hard short in the electrochemical energy devices during operation has caused serious safety problems such as rapid temperature rise or explosion, because the internal short occurs at a very small contact area between two electrodes in the electrochemical energy devices and the large current and high resistance cause rapid temperature rise or even explosion.[48, 49] In contrast, the IS pre-doing here had very wide area of physical contact between electrodes, which facilitated dissipation of reaction heat generated during lithium intercalation in the excess electrolyte and excluded the safety concern.

Conclusions

In summary, it was demonstrated that the IS approach is a fast and efficient process for the lithium pre-doping in the lithium-ion capacitors. Direct contact between graphite electrode and lithium metal leads to very fast but controllable lithium pre-doping into the graphite due to the large contacting area in the excess electrolyte medium facilitated not only fast lithium interaction into graphite but also fast dissipation of reaction heat generated during this lithium intercalation process. The AC/graphite full-cells pre-doped through IS method exhibit remarkably higher coulombic efficiency and longer cycle life than the cells prepared with conventional EC and ESC pre-doping methods. Therefore, the IS pre-doping approach is an ease and efficient way to significantly improve the anode manufacturing speed and reduce the cost of the high energy density lithium-ion capacitors.

Acknowledgements

Notes

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