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Regeneration of Fully-discharged Graphite-Fluoride Lithium Primary Battery as Electrochemical Capacitor

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ABSTRACT

This paper reports that the fully-discharged graphite-fluoride Li primary battery (GF/Li battery) can be regenerated as a hybrid capacitor with a higher energy density than the electric double layer capacitor (EDLC) using an activated carbon electrode. The graphite-fluoride (GF) positive electrode of the GF/Li battery is electrochemically defluorinated during the fully-discharged process to be converted to a nanocomposite consisting of carbon and LiF particles. The nanocomposite as the discharge product behaves as a capacitor-like electrode, so the fully-discharged GF/Li battery can be stably charged/discharged as a hybrid capacitor with the capacitor-type electrode (defluorinated GF electrode) and the battery-type negative electrode (Li metal). This hybrid capacitor, i.e., "graphite-fluoride Li capacitor (GF/Li capacitor)", exhibited the maximum volumetric energy density of 52 Wh L^{-1} (at the power density of 71 W L^{-1}), which is higher than that of the EDLC and comparable to that of the Li-ion capacitor. In this paper, the improvement of the cyclability by using the graphite/Li bilayer negative electrode and the charge-discharge mechanism are also discussed for the GF/Li capacitor.

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Keywords : Graphite-fluoride, Li Battery, Defluorination, Hybrid Capacitor

1. Introduction

In response to social energy and environmental issues, there are needs for the creation and utilization of clean energy sources that have a low environmental load. The electric energy storage/conversion devices, such as electrochemical capacitors (ECs), rechargeable batteries and fuel cells, have been expanded in the applications from mobile devices to the hybrid and/or electric vehicles and the storage system of the renewable energies.^{1,2} An excellent energy density and power density are currently required to facilitate the use of these technologies.

The ECs have attracted much attention due to their excellent power density and long cycle life compared to rechargeable batteries.^{3–5} The electric double layer capacitor (EDLC), which is the first-commercialized EC, is charged-discharged by a non-faradaic process (ion adsorption/desorption) on the electric double layer formed at the interface of the electrolyte and porous carbon (ex. activated carbon) electrode surface. The EDLCs have been utilized as the memory back-up power supply for mobile devices since the 1970s and recently have been applied as the power-assist systems for the hybrid vehicle, etc. However, the energy density of the EDLC is much lower than that of the rechargeable batteries, so the hybrid capacitor (HC), which is the EC using different types of materials for the positive electrode and negative electrode, was developed to increase the energy density of the ECs. The Li-ion capacitor (LIC) is a commercialized HC, which combines the positive electrode (porous carbon) used for the EDLC and the negative electrode (Li pre-doped carbon) for the Li-ion battery.^{6,7} The LIC exhibits high energy and power densities based on its charge-discharge mechanism in which the electric energy is stored in the LIC by adsorption-desorption of the electrolyte-ions at the

positive electrode and electrochemical intercalation-deintercalation of Li at the negative electrode.⁷

In both the EDLC and the LIC, porous carbons are the key materials to determine the capacitance of the devices. Generally, activated carbons as representative porous carbons for the ECs are manufactured by a gasification (activation) process of carbon with steam, CO_2 , and chemical reagents, such as KOH or NaOH.^{8,9} However, the porous carbons with a high surface area and capacitance can also be prepared by other techniques than the activation method. For example, the author (S.S) found that the meso/microporous carbons derived from the defluorination of polytetrafluoroethylene (PTFE) show a high capacitance and rate performance compared to the conventional activated carbons.^{10–13} PTFE is electrochemically defluorinated with alkali metals (ex. Li, Na, K), their amalgam, or their naphthalenide to be converted to a nano-composite consisting of carbyne (sp-hybridized carbon allotrope)-like structure and alkali metal fluorides (MF, such as LiF, NaF, and KF).^{14,15} The nano-composite as the PTFE defluorination product is very chemically unstable due to cross-linkage of the sp-hybridized carbons and aggregation of the MF nanoparticles, but generates meso/microporous carbons through the MF removal by water or acid without utilizing the conventional gasification process.^{15,16} Moreover, the author (S.S) revealed that graphite-fluoride (GF), which is a covalent-type graphite intercalation compound (GIC), can be defluorinated with Li-naphthalenide to obtain lamelliform carbon with a moderate specific surface area ($\sim 200 \text{ m}^2 \text{ g}^{-1}$).^{17,18} The GF-derived lamelliform carbon shows a higher volumetric capacitance than conventional activated carbons in a typical organic electrolyte for the EDLC. Thus, it can be said that the defluorination of fluorocarbons is an attractive preparation method for the porous carbon electrode of the ECs.

Figure 1. Schematic illustrations of the first-discharge reaction mechanism of the GF/Li battery and the concept of regeneration of the fully-discharged GF/Li battery as a hybrid capacitor (in the case of only the Li^+ cation contributing to the charge-discharge process).

Based on the previously described research, the authors focused on the first-discharge product of the positive electrode in the graphite-fluoride Li primary battery (GF/Li battery). According to the literature,^{19,20} the first-discharge reaction of the GF/Li battery was simply described as follows.

Positive electrode: $(CF)_n + nLi^+ + ne^- \rightarrow nC + nLiF$

Negative electrode: $Li \rightarrow Li^+ + e^-$

The discharge reaction is the electrochemical defluorination of GF and the discharge product is a nanocomposite of carbon and LiF,²¹ which is very similar to the defluorination product of GF with Li-naphthalenide. If the discharged GF electrode could behave as the capacitor-type electrode, the fully-discharged GF/Li battery should be regenerated as the HC with a capacitor-type positive electrode (GF-defluorinated product) and battery-type negative electrode (Li metal). The HC derived from the fully-discharged GF/Li battery is expected to exhibit a high energy and power density as well as the LIC. The schematic illustrations of the first-discharge reaction and the concept of the regeneration for the GF/Li battery as the HC are shown in Fig. 1. Based on this concept, it is illustrated that the fully-discharged GF/Li battery is charged or discharged as the HC by the adsorption-desorption of the electrolyte-ions at the positive electrode and the electrochemical deposition-dissolution of Li metal at the negative electrode.

In this paper, the authors demonstrate the characteristic HC based on the regeneration (charge process) of the used (fully-discharged) GF/Li primary battery as a capacitor and report the basic electrochemical performance and the charge-discharge mechanism.

2. Experimental

2.1 Materials and electrochemical measurements

The GF test electrode was fabricated by coating an etched-aluminum foil current collector (Japan Capacitor Industrial Co., Ltd.) with a slurry composed of the GF powder (electrode active material, CEFBON CMC, average particle diameter of 5 μm , C : F = 1 : 1.12, Central Glass Co., Ltd.), acetylene black as the conductive material (Denka Co., Ltd.), and polyvinylidene fluoride (PVdF) binder (L#9305, Kureha Corp.) in the mass ratio of 8 : 1 : 1.

Figure 2. A two-electrode cell configuration (positive electrode side: Al body, negative electrode side: stainless steel body) of the GF/Li battery consisting of the GF positive electrode, the Li metal negative electrode, the polyolefin-based separator, and 1 M $LiPF_6$ /(EC+EMC) electrolyte.

The test electrode was pressed for 2 min at $400 kgfcm^{-2}$ and the disk-like electrode with a diameter of 15.5 mm was punched out. The loading mass of the GF was about 10–11 mg, and the GF test electrode bulk density was also about $1.4 gcm^{-3}$. Prior to the electrochemical measurement, the GF test electrode was dried for 2 h at 200 $^{\circ}C$ in a vacuum.

A two-electrode test cell of the GF/Li battery (Fig. 2) was assembled with the GF test electrode as the positive electrode, Li metal foil (0.48 mm or 0.03 mm, Honjo Metal Co., Ltd.) or bilayer

sheet of graphite/Li metal as the negative electrode, a polyolefin-based separator, and 1 mol dm⁻³ lithium hexafluorophosphate (LiPF₆) containing ethylene carbonate and ethyl methyl carbonate mixed solution (EC+EMC, 3 : 7 v/v, Tomiyama Pure Chemical Industry, Ltd.) as the electrolyte. The bilayer sheet of graphite/Li metal was prepared by pressing Li metal foil (0.03 mm) and graphite composite film (0.02 mm) composed of graphite powder (KS-44, TIMCAL, Ltd.) and PVdF binder (9 : 1 in mass ratio). The relationship of the capacity between each electrode active material is summarized in Table S1. For all GF/Li battery cells, the capacity of the negative electrode is higher than that of the positive GF electrode.

The battery and capacitor properties of the test cell were evaluated by an auto charge-discharge unit (HJ1001SM8A, Hokuto Denko Corp.). The first-discharge (lower cut-off cell voltage: 1.5 V) and subsequent charge-discharge cycle tests (voltage range: 2–4 V) of the cell were carried out by the galvanostatic method (current density of 40 mA g_{PE}⁻¹ or 400 mA g_{PE}⁻¹). The Ragone plot of the cell as the HC was obtained by the constant power discharge (4 → 2 V) at various constant powers.

2.2 Scanning electron microscopy and X-ray diffraction measurements

The surface morphologies of the pristine and tested GF positive electrodes were observed by a scanning electron microscope (SEM) of a JSM-6510AS instrument (JEOL Ltd.) at the acceleration voltage of 10 kV. The X-ray diffraction (XRD) for the GF powder, the pristine GF positive electrode, and the tested GF test electrode was conducted using a RINT2100V/PC (Rigaku Co., CuK α radiation; 32 kV, 20 mA) at $2\theta = 5\text{--}90^\circ$, a scanning rate of 1°min^{-1} . The tested electrode was carefully washed by pure propylene carbonate and dimethyl carbonate (Battery Grade, Kishida Chemical Co., Ltd.) prior to the SEM and XRD analyses. For the XRD analysis, the tested electrode was covered with polyimide (Kapton®) film to prevent the electrode from reacting with air.

2.3 Inductively coupled plasma optical emission spectroscopy & ion chromatography

The inductively coupled plasma optical emission spectroscopy (ICP-OES) and ion chromatography (IC) were conducted to discuss the electrolyte-ion species contributing to the charge-discharge process of the fully-discharged GF positive electrode. The amounts of elemental Li and P contained in the fully-discharged GF positive electrode were determined by the ICP-OES analysis using a Spectro Blue (SPECTRO Analytical Instrument, Inc.). The amount of F⁻ anion in the electrode was also quantified by IC analyses using an IC-2001 (Tosoh Corp.). More details of the analytical condition are described in the Supporting Information.

2.4 Electrochemical quartz crystal microbalance (EQCM) analysis

4 mg of the GF powder was dispersed in 20 mL of ethanol by ultrasonication for 5 min to prepare the GF dispersion. 20 μ L of the dispersion was spin coated onto an Au-coated AT-cut QCM electrode (13.3 mm², 6 MHz, Hokuto Denko Corp.), then dried at 60 °C. Excess sample outside the working electrode area of the QCM electrode was carefully wiped off. A series of these loading processes was performed twice to uniformly load a sufficient amount of GF on the QCM electrode. The prepared GF (ca. 6 μ g)-loaded QCM electrode was dried for 2 h at 200 °C in a vacuum before the EQCM measurement. In an argon glove box, the GF-loaded QCM electrode was placed in the EQCM cell, and the EQCM analysis with the QCM analyzer (QCA922, Seiko EG&G Co.) and the auto charge-discharge unit (HJ1001SM8A, Hokuto Denko Corp.) was carried out. A propylene carbonate solution containing 1 mol dm⁻³ lithium tetrafluoroborate (LiBF₄/PC) as the electrolyte, Li metal as

the counter electrode, and Li/Li⁺ as the reference electrode were used in the EQCM three-electrode cell. The electrochemical reduction (corresponding to the first discharge process for the GF/Li battery) of the GF-loaded QCM electrode was conducted from the open circuit potential (around 3 V vs. Li/Li⁺) to 1.5 V vs. Li/Li⁺ by a galvanostatic method (current value of 10 μ A). Chronopotentiometry (corresponding to the charge-discharge process in the constant current mode for the regenerated capacitor) was then carried out at a constant current (10 μ A) in the electrode potential direction of 2 → 4 V or 4 → 2 V vs. Li/Li⁺, and this process was repeated 10 times. The mass change of the GF-loaded QCM electrode was evaluated from the resonance frequency change during the charge-discharge process using Sauerbrey's equation (Eq. 1).²²

$$\Delta f_m = \frac{-2f_0^2}{A\sqrt{\mu_q\rho_q}} \quad (1)$$

Where, A is the working electrode area of the QCM electrode (1.33 cm²), μ_q is the elastic modulus of quartz (2.95×10^{11} g cm⁻¹ s⁻²), ρ_q is the density of quartz (2.648 g cm⁻³), and f_0 is the fundamental resonance frequency of the QCM electrode (6 MHz). Thus, the resonance frequency change of 1 Hz corresponds to the mass change of 16.3 ng in this EQCM system.

3. Result and Discussion

3.1 Charge-discharge behavior

Figure 3 shows the first-discharge curve of the GF/Li battery and the charge-discharge curve of the fully-discharged GF/Li battery. During the first-discharge process, the GF/Li battery exhibits the typical battery-type plateau discharge curve around 2.5 V, which is in good agreement with the literature.²¹ The charge-discharge curves with a triangular shape were observed for the subsequent charge-discharge cycles after the first discharge, which means that the fully-discharged GF/Li battery cell works as a capacitor. The charge-discharge curve at the 50th cycle also preserved the triangular shape, as shown in Fig. 3b. The gravimetric and volumetric capacitances calculated from the discharge curve slope and the weight and volume of the positive electrode were around 34 F g⁻¹ and 48 F cm⁻³, respectively. Those of the activated carbon composite electrode prepared using the typical activated carbon powder (YP50F, Kuraray, Co., Ltd.) for the EDLC were around 50 F g⁻¹ and 30 F cm⁻³ under the same conditions using the two-electrode cell of the YP50F positive electrode and Li metal negative electrode, respectively. The volumetric capacitance for the GF electrode was higher than that for the activated carbon electrodes. Thus, it was confirmed that the fully-discharged GF/Li battery can be regenerated as the HC by the subsequent charge-discharge. Hereafter, the authors refer to this HC derived from the fully-discharged GF/Li battery as the “graphite-fluoride Li capacitor (GF/Li capacitor)”.

The electrochemical impedance spectra (Nyquist plots) of the GF/Li battery cell, the fully-discharged cell, and the GF/Li capacitor are shown in Fig. S1. The characteristic frequency at the top of the observed semicircle for each cell is also summarized in Table S2. The internal resistance estimated by the semicircle attributed to the charge-transfer resistance or contact resistance of the active materials and current collector, decreased with the discharging depth of the GF/Li battery. This indicated that the electrical conductivity of the electrode was improved due to the insulator part (GF powder) decreasing by the first-discharge reaction. Moreover, the GF/Li capacitor shows the lowest internal resistance compared to the pristine, the slightly discharged, and the fully-discharged GF/Li batteries. Therefore, the GF/Li capacitor can be considered to act as a high rate device compared to the GF/Li battery.

Figure 3. (a) The first-discharge curve (battery-like) and the subsequent charge-discharge curves (capacitor-like) of the GF/Li battery cell, (b) the 50th charge-discharge curve of the fully-discharged GF/Li battery cell (GF/Li capacitor) by a galvanostatic method (current density of $40 \text{ mA g}_{\text{PE}}^{-1}$). The Li metal with a thickness of 0.48 mm was used as the negative electrode for the GF/Li battery.

3.2 Electrode characterization before and after the first discharge

Figure 4 shows SEM images of the pristine and tested GF electrodes (after the 30 charge-discharge cycles). GF flakes with a submicron particle size and carbon black nano-particles were observed in the pristine GF electrode. The surface of the tested electrode is rough compared to the pristine electrode, which can be due to the expansion of the GF flakes by the discharge reaction (Li^+ cation is incorporated into the electrode matrix), but the morphology was not essentially different. Thus, these SEM images indicated that the discharged GF positive electrode was apparently stable as a capacitor electrode since the active material particles were not pulverized by the charge-discharge cycles.

Figure 5 shows XRD patterns of the GF powder, the pristine GF electrode, and the tested GF electrode. The XRD profiles of the GF powder and the pristine GF electrode showed the diffraction peaks attributed to the (001) and (10) planes of stage I of the GF around the 2θ values of 12° and 41° , respectively. The d-spacing of the (001) plane (d_{001}) was calculated to be around 0.71 nm . These are in good agreement with the literature.^{23,24} In the pristine GF electrode (Fig. 5b), the broadened small peak around the 2θ value of 26° and sharp peaks around the 2θ values of 66° and 78° were also observed, which can be assigned to the (002) plane of acetylene black and Al current collector, respectively. The XRD profile of the fully-discharged GF test electrode (Fig. 5c) showed that the (001) peak of

Figure 4. SEM images of (a, b) the pristine GF electrode, and (c, d) tested GF electrode after the 30 charge-discharge cycles.

Figure 5. XRD profiles of (a) the GF powder, (b) the pristine, (c) first-discharged GF positive electrodes, and (d) the Kapton® film. * Al current collector.

GF disappeared and the new peaks attributed to LiF (111), (200), and (220) appeared. The crystallite size (L_{200}) of the LiF calculated by Sherrer's equation is around 7 nm . A very broadened peak of low-crystalline carbon around the 2θ value of $15\text{--}25^\circ$ was also observed although the profiles (Fig. 5d) of the polyimide film overlapped with that of the carbon. These profiles confirmed that the electrochemical defluorination reaction of GF occurred during the fully-discharged reaction to produce the composite of carbon and small LiF particles as discussed in the literature.^{19–21} Thus, it can be considered that the nanocomposite of carbon and LiF as the discharged products of the GF positive electrode can function as a capacitor-type electrode in spite of the presence of the insulating LiF as well as the defluorinated PTFE electrode.²⁵

3.3 Charge-discharge mechanism

To discuss the charge-discharge mechanism of the GF/Li capacitor in detail, the ICP-OES and IC were carried out for the tested GF positive electrode. Figure 6 shows the relationship

Figure 6. Theoretical (dotted line) and experimental (solid line) Li/F and P/F atomic ratio of the tested GF positive electrode in the GF/Li capacitor at the cell voltage of 2 V, 3 V, or 4 V.

between the Li/F and P/F atomic ratio contained in the tested GF electrode and the cell voltage of 2 V (the discharge-state), 3 V (around initial open circuit voltage) or 4 V (the charge-state) for the GF/Li capacitor. The P/F ratio was ca. 0.013 and almost not independent of the cell voltage, which means that the PF_6^- anion does not contribute to the charge-discharge process. In the case of the Li/F, the atomic ratio was almost 1, corresponding to the stoichiometry of LiF, but the ratio decreased with the cell voltage. This suggests that only the Li^+ cation is related to the charge-discharge process for the positive electrode of the GF/Li capacitor. Additionally, the theoretical line (red-dotted) for the Li/F ratio, calculated from the amount of passed electricity for the charge under the assumption that a Li^+ cation is undoped into the electrode by extracting an electron during the charge process, was roughly consistent with the experimental one. Meanwhile, the theoretical line (blue-dotted) calculated for the PF_6^- anion in the same manner of the Li^+ cation did not coincide with the result of the P/F ratio. Thus, it can be considered that the Li^+ cation is the main active species desorbed during the charge process (2 $\rightarrow$ 4 V) and adsorbed during the discharge process (4 $\rightarrow$ 2 V) for the nanocomposite electrode consisting of carbon and LiF.

Figure 7 shows the chronopotentiogram and the mass change of the electrochemically reduced GF-loaded QCM electrode at the 10th cycle of the positive and negative polarization process in the potential range of 2–4 V vs. Li/Li^+ . These data correspond to the electrochemical behavior during the charge and discharge process for the positive electrode of the GF/Li capacitor as described in the experimental section. The electrode mass decreased with the positive polarization while it increased with the negative polarization.

Based on the EQCM analysis, the mass change related to the anion and cation adsorption/desorption are observed for the activated carbon electrode for the EDLC.^{26–28} Thus, for the positive electrode (C and LiF) for the GF/Li capacitor, it is also expected that the anion is adsorbed/desorbed in the potential region of 3–4 V vs. Li/Li^+ and that the cation is adsorbed/desorbed in the region of 2–3 V vs. Li/Li^+ if the pzc is ca. 3 V vs. Li/Li^+ as well as that of the activated carbon. However, in the case of the positive electrode for the GF/Li capacitor, the observed mass changes suggest that only the Li^+ cation is desorbed during the positive polarization (charge process) and that it is adsorbed during the negative polarization (discharge process). To verify this idea, the theoretical line of the mass change was also calculated from the atomic weight of Li (M_{Li} : 7) and the amount of electricity passed during the positive or negative polarization in the same manner at the ICP-OES analysis.

Figure 7. Chronopotentiogram and mass change of the electrochemically reduced GF-loaded QCM electrode in the potential range of 2–4 V vs. Li/Li^+ by a galvanostatic method (current value of 10 μA). The blue line, red line, or black dot line is potential curve, observed mass change, or theoretical mass change (assuming that only the Li^+ cation is adsorbed/desorbed) of the GF-loaded QCM electrode, respectively.

The theoretical line is consistent with the observed mass change as shown in Fig. 7.

Therefore, based on these results of the ICP-OES, IC, and EQCM analyses, it was revealed that the GF/Li capacitor is mainly charged or discharged by the adsorption-desorption of the Li^+ cation. However, the discharge product of the GF electrode (nanocomposite of carbon and LiF) was not microporous since the BET specific surface area was less than $100\text{ m}^2\text{ g}^{-1}$ as shown in Fig. S2 and Table S3. This suggests that the Li^+ cation adsorption-desorption path and system in the defluorinated GF is similar to that of the electrochemical activation type of carbon electrode with a low specific surface area^{29,30} which is different from that of the conventional activated carbon with a high specific surface area. For example, it can be speculated that the Li^+ cation diffuses between the LiF nanoparticles and adsorbs the surface of the small-sized carbon crystallite with wide interspace.

3.4 Cycle performance

Figure 8 shows the cycle performance of the GF/Li capacitor using a Li metal negative electrode or graphite/Li metal bilayer negative electrodes. For the use of only Li metal as the negative electrode material, the capacitance of the GF/Li capacitor rapidly decreased around the 60th cycle. It is due to accumulating the electrochemically inactive dendritic Li by repeating the charge-discharge cycle. A very low cycle performance for rechargeable batteries using Li metal has been widely known.^{31,32}

To improve the cyclability, the authors used the bilayer electrode consisting of graphite and lithium metal as the negative electrode. In this bilayer negative electrode, the graphite layer changes into Li-GIC in the electrolyte containing the Li^+ cation.³³ For the GF/Li battery with the bilayer negative electrode, it was also confirmed that the Li-GIC was formed during the first-discharge process as shown in Fig. S3. The fully-discharged GF/Li battery with the bilayer negative electrode also works as a capacitor as well as that with the usual Li metal negative electrode as shown in Fig. S4. Furthermore, the Li-GIC in the bilayer negative electrode has higher capacity (1.1 mAh) than the positive electrode (0.6 mAh) of the GF/Li capacitor as shown in Table S1.

In the case of the GF/Li capacitor using the bilayer negative electrode, the cyclability was significantly improved as shown in Fig. 8. The initial capacitance was maintained even after more than

Figure 8. Cyclability of the GF/Li capacitor using a Li metal negative electrode or graphite/Li metal bilayer negative electrode at the current density of $400 \text{ mA g}_{\text{PE}}^{-1}$, the operating cell voltage range of 2–4 V. The volumetric capacitances of the GF/Li capacitor were normalized with the total volume of both positive and negative electrodes.

Figure 9. Ragone plots of the GF/Li capacitors (cell voltage: 2–4 V), the EDLC (cell voltage: 1.5–3 V), and the LIC (cell voltage: 2–4 V). The fabrications of the ECLC and the LIC cells are described in Supporting Information.

5000 charge-discharge cycle tests. This indicated that in the GF/Li capacitor, the Li-GIC operates as the reversible negative electrode based on the electrochemical Li intercalation and deintercalation. Therefore, it can be said that the bilayer structure of the negative electrode (graphite/Li metal) is very effective to improve the cycle performance of the GF/Li capacitor.

3.5 Energy density and power density

Figure 9 shows the Ragone plot of the GF/Li capacitor using only Li metal or the bilayer electrode as the negative electrode, the LIC, and the conventional EDLC using a commercially-activated carbon electrode. Using only Li metal as the negative electrode, the maximum volumetric energy density of the GF/Li capacitor reached 52 Wh L^{-1} at the power density of 71 W L^{-1} . This value is three-times higher than that of the EDLC, and close to that of the LIC. The maximum volumetric energy density for the GF/Li capacitor using the bilayer negative electrode was lower than that of the LIC and the GF/Li capacitor using a Li metal negative electrode. This decrease in the energy density is related to the additional weight and volume

of the graphite film layer. However, the energy density at a higher power density (around 10000 W L^{-1}) for the GF/Li capacitor using the bilayer electrode is comparable to that of the LIC and the GF/Li capacitor using a pristine Li metal electrode. Therefore, it is concluded that the bilayer structure of the graphite film and Li foil is suitable for the GF/Li capacitor although the energy density of the capacitor cell should be further improved.

4. Conclusion

This paper demonstrated that the fully-discharged Li primary battery using graphite-fluoride as the positive electrode active material operates as a hybrid capacitor denoted as “graphite-fluoride Li capacitor (GF/Li capacitor)”. The GF/Li capacitor exhibits a higher volumetric energy density and power density than the EDLC and comparable performance to the LIC. The drawback for the GF/Li capacitor is its poor cyclability due to the Li metal dendrite deposition, but is markedly improved by using the bilayer negative electrode composed of the graphite composite film and Li metal. The inductively coupled plasma optical emission spectroscopy, ion chromatography, and electrochemical quartz crystal microbalance indicated that the charge-discharge mechanism for the positive electrode of the GF/Li capacitor is the adsorption-desorption of the Li^+ cation in the nanocomposite of carbon and LiF which is the first fully-discharged product at the positive electrode of the GF/Li battery.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-65131>.

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