



Formation of holes into granule $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode for enhanced performance of hybrid supercapacitors

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ARTICLE INFO

Article history:

Received 14 September 2017

Received in revised form

7 November 2017

Accepted 7 November 2017

Available online 10 November 2017

Keywords:

Hybrid supercapacitors

Punched granule $\text{Li}_4\text{Ti}_5\text{O}_{12}$

High power anode

Long-term cycling

Electrolyte impregnation

ABSTRACT

Hybrid supercapacitors are being studied as a next-generation energy storage device that bridge supercapacitor and lithium-ion battery. However, an imbalance of two electrodes of hybrid supercapacitors, especially due to the slow lithium ion kinetics at anode is the one of the most important problems. To solve this problem, we have demonstrated optimized hybrid supercapacitor performance by applying the punched granule $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (P-LTO) via mechanical punching as a high power anode. The hybrid supercapacitors based on P-LTO anode and activated carbon delivers not only high specific capacity of 57 F/g and excellent long-term cycling of 99% after 14,000 cycles but also remarkable rate capability of 90.6% even at a high rate of 4 A/g, mainly due to i) increase in the total effective contact area, ii) efficient electrolyte impregnation and iii) effective dispersion of hydrogen fluoride attack.

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1. Introduction

With the development of electric vehicles, renewable energy and portable devices, the interest in high-performance energy storage devices has been increased. Although the supercapacitors and lithium ion batteries (LIBs) have been widely used as a power source in various application fields [1,2]. However, the two existing energy storage devices have fatal disadvantages of low energy density (supercapacitors) and poor power density, short cycle life (LIBs), respectively. They have ultimately limitations to meet all the requirements of energy storage devices. Elon Musk, Tesla's CEO, insisted that the future of electric vehicles is more dependent on the development of advanced supercapacitors than lithium-ion batteries due to excellent power density and cycle performance without capacitance loss [3]. However, the electric vehicle based on supercapacitors as a power source have not been commercialized yet. It can be elucidated by insufficient energy density from 20 to

50 Wh/kg of supercapacitor, although it has a superior power density of 3 kW/kg or more [4].

Recently, the asymmetric hybrid supercapacitors, which is generally comprised of battery-type transition metal oxide anode and capacitive carbon-based cathode, are widely regarded as a potentially game-changing energy storage device to enable extraordinary electrochemical performances, including not only high energy and power densities but also long cyclability. However, the hybrid supercapacitors also have several problems that need improvement. One of the most important problem of hybrid supercapacitors is the imbalance between anode and cathode, mainly due to anode, resulting from different capacity mechanisms [5]. Among anode material candidates, the spinel LTO can be considered to be one of the promising anode materials by following reasons: i) zero strain insertion materials and ii) high redox potential (1.55 V vs Li/Li^+), resulting in superior cycling performance. iii) much higher theoretical LTO can capacity of 175 mAh/g than that of activated carbon (AC), which is an electrode for supercapacitors [6]. Therefore, compared to other anode candidates such as NiO , NiCo_2O_4 , $\text{H}_2\text{Ti}_{12}\text{O}_{25}$ and TiO_2 has been widely studied, however, LTO is the most suitable for real application. This is because LTO anode can improve the energy density without

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sacrificing the cycle life, which is the most important factor to meet the requirement of hybrid supercapacitors [7–10].

Nevertheless, relatively slow kinetics of lithium ion and gas generations of anode degrade the performance of hybrid supercapacitors. To solve these problems, in this paper, the fine granule $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) with a porous microstructure are designed. Furthermore, we prepared P-LTO to maximize electrochemical performances of hybrid supercapacitors. Due to the combination of P-LTO anode and AC cathode, the fabricated hybrid supercapacitors delivers outstanding electrochemical performances.

2. Experimental

Granule LTO powders were fabricated by spray drying process with precursor slurry and subsequently calcined in air at 800 °C for 6 h. The precursor slurry was prepared from Li_2CO_3 (Junsei, 98%), TiO_2 (Junsei, 99.0%) as raw materials. The molar ratio of lithium ion and titanium oxide was 4:5. The powders were mixed in ethyl alcohol for 24 h in a ball mill. The homogenous slurry was atomized at the temperature of 200 °C using a two-fluid nozzle with atomizing pressure of 3.5 kg/cm².

The hybrid supercapacitor was composed of the LTO anode and activated carbon (AC) cathode. An AC cathode was fabricated by mixing AC (MSP-20, 90 wt%) with conductive carbon (5 wt%) and polytetrafluoroethylene (PTFE, 5 wt%). In order to fabricate the anode, LTO powder, conductive carbon black binder (Super P), and polyvinylidene fluoride (PVDF) were mixed in an 83:7:10 wt ratio. N-Methyl pyrrolidine (NMP) solvent was added to produce the slurry. The masses of cathode and anode were 3.4 g and 3.3 g, respectively. This was casted on aluminum foil to a thickness of 125 μm and then dried at 100 °C to remove the NMP solvent. The aluminum foil was pressed to a thickness of 70–80 μm and then the LTO sheets was punched, as shown in Fig. 1. The electrodes of full-cells were prepared by the above-stated method and full-cells were assembled with using P-LTO as an anode and activated carbon as a cathode in argon-gas-filled glove box. The width of the cathode, separator, and anode were 28 cm, 40 cm, and 30 cm, respectively and the heights of the cathode and anode were both 3 cm. Before being impregnated with a 1.5 M solution of LiPF_6 solution in 1:1 ethylene carbonate (EC): dimethyl carbonate (DMC) as the electrolyte, in order to remove the moisture in the cell, the fabricated cell was dried in a vacuum oven for 48 h.

The structure of P-LTO was analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) was used to observe the punched hole of LTO. The cyclic voltammograms (CVs) were measured using a potentiostat (lviumstat) and electrochemical impedance spectroscopy (EIS) was conducted using a CHI660D electrochemical workstation in the frequency range of 10^{-1} to 10^3 Hz. The electrochemical measurement of the fabricated

cell was carried out with various tests, such as initial capacitance and rate capability, using an Arbin BT 2042 battery test system.

3. Results and discussion

Fig. 2(a) shows the XRD pattern of the P-LTO. The crystal structure of P-LTO is a spinel structure with space group of $\text{Fd}\bar{3}\text{m}$. The diffraction peaks can be indexed to (111), (311), (400), (331), and (511) reflections, corresponding to those of granule LTO, while no secondary phase was observed [6,7]. Therefore, it can be deduced that P-LTO anode was well synthesized for hybrid supercapacitors anode. The granule LTO shows a size of about 5 μm , which is comprised of primary particles with average size of 400 nm, as shown in Fig. 2(b) [6]. Fig. 2 (c) shows the SEM images of the P-LTO sheet (i). For detailed information on hole microstructure, the enlarged SEM images of punched hole were measured. We can confirm that the diameter of punched hole was 80.50 μm (ii). Also, the depth of punched hole was 64.51 μm which is measured after FIB drilling (iii). It indicates that the punched structures were well prepared on the surface of granule LTO sheet. Therefore, it can be inferred that the P-LTO can affect the electrochemical performances of the hybrid supercapacitors.

Fig. 3 shows the cyclic voltammetry (CV) curves of the hybrid supercapacitors using P-LTO and granule LTO over the voltage range of 0–2.8 V due to the operating voltage of 4.3 V for the AC cathode and 1.5 V for the LTO. Both CV curves had the identical shape and showed a curve of a typical hybrid supercapacitor. The hybrid supercapacitors were hybridized the two different electrodes: i) LTO which store charge by Faradaic mechanism (redox reaction) above 1.5 V and ii) AC which store charge by non-Faradaic mechanism (capacitive behavior) between voltage ranges of 0 V and 2.8 V [11]. The redox peaks of the hybrid supercapacitor including a pair of anodic and cathodic peaks ranged from 2.3 to 2.8 V. It is noteworthy that the area surrounded by the CV curve of P-LTO is similar to that of granule LTO at a scan rate of 5 mV/s, demonstrating almost the same electrochemical activity. More importantly, we can confirm that both hybrid supercapacitors have similar polarization value, which is closely related to reversibility from anodic and cathodic peak according of the CV curves by the following equation [1]:

$$\Delta\phi = (\phi_a - \phi_c)/V \quad (1)$$

where ' ϕ_a ' is the anodic peak, ' ϕ_c ' is the cathodic peak, and ' $\Delta\phi$ ' is the polarization difference between the anodic and cathodic peak potentials.

In hybrid supercapacitors, the polarization is mostly dependent on the anode due to slow kinetics of lithium ion than that of cathode. The anodic and cathodic peaks of P-LTO and granule LTO

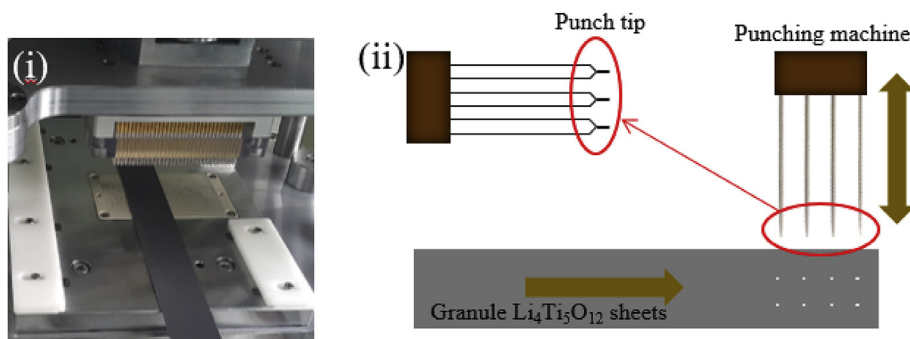


Fig. 1. Photograph and Schematic diagram of punching system.

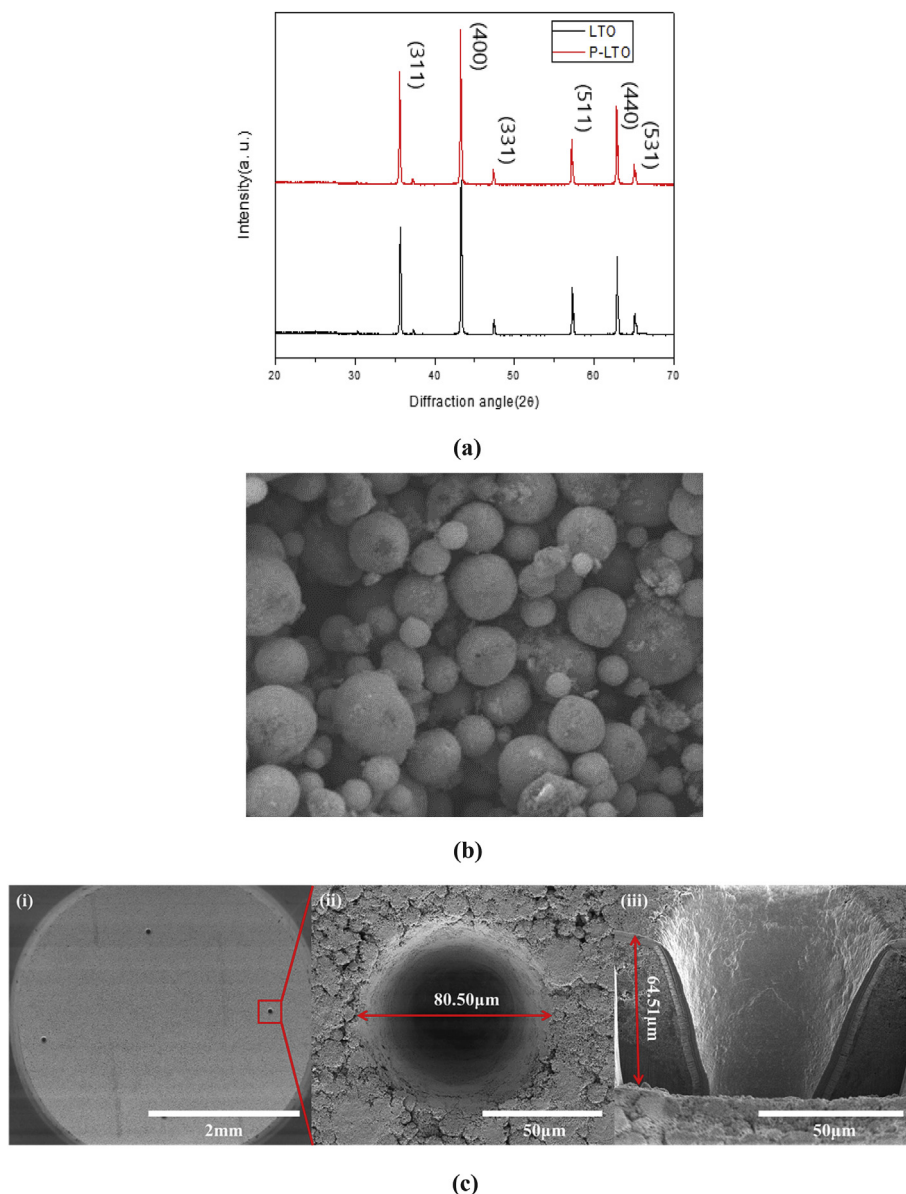
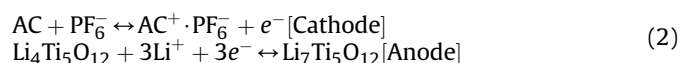


Fig. 2. (a) XRD patterns of granule LTO and P-LTO. SEM images of (b) granule LTO (c) P-LTO.

are nearly identical at a slow scan rate of 5 mV/s. Therefore, we can conclude that the small polarization of P-LTO and granule LTO, derived from effective lithium ion intercalation between electrolyte and anode, demonstrates relatively faster kinetics of lithium ion during charge-discharge process [12,13].

Fig. 4 shows the initial charge-discharge curves of hybrid supercapacitors between 1.5 and 2.8 V due to its cut-off voltage of 1.5 V. The different charge storage mechanism between P-LTO anode and AC cathode can be expressed from following reaction [14]:



As expected, the P-LTO shows a nearly same discharge capacitance that of granule LTO. The discharge specific capacitances of the hybrid supercapacitors using P-LTO, HTO can be calculated by the following equation [4]:

$$C = \frac{q}{\Delta V \times m} = \frac{\int i \Delta t}{\Delta V \times m} \quad (3)$$

where 'C' is the capacitance (Fg^{-1}), ' ΔV ' is the voltage change, 'm' is the mass of the active materials in both electrodes, 'q' is the total charge, 'i' is the current, and 't' is time. The small difference is due to the relatively slow current density of 1 A/g. Therefore, we can confirm that granule LTO also has a sufficiently high capacitance at slow current density due to sufficiently fast lithium ion kinetics. However, discharge capacitance of P-LTO is a little higher, and the values of P-LTO and granule LTO are 53 and 57 F/g, respectively. It can be explained by wider contact area, derived from punched structure for obtaining high capacitance of hybrid supercapacitors.

A sudden drop in voltage, named IR (current $\times$ resistance) drop can be observed at the beginning of discharge curves in both hybrid supercapacitors, meaning low internal resistance. The IR drop can be calculated by the following equation [3]:

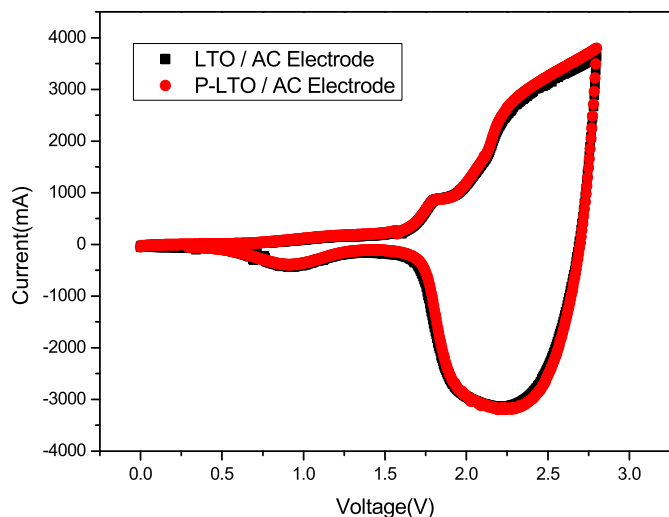


Fig. 3. CV curves of LTO and P-LTO at a scan rate of 5 mV/s.

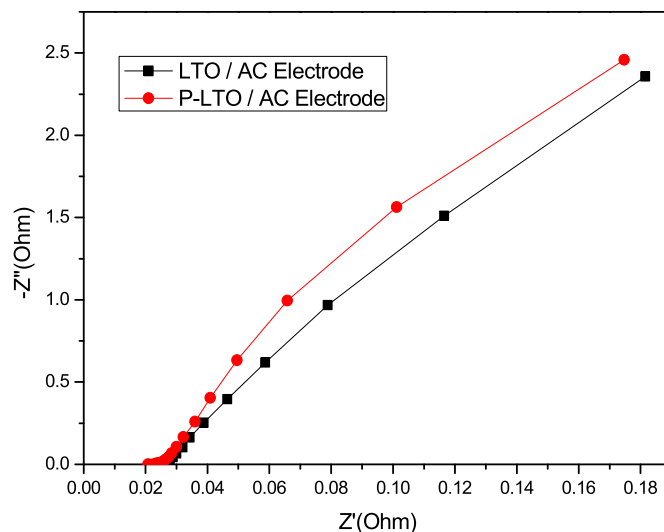


Fig. 5. EIS curves of LTO and P-LTO.

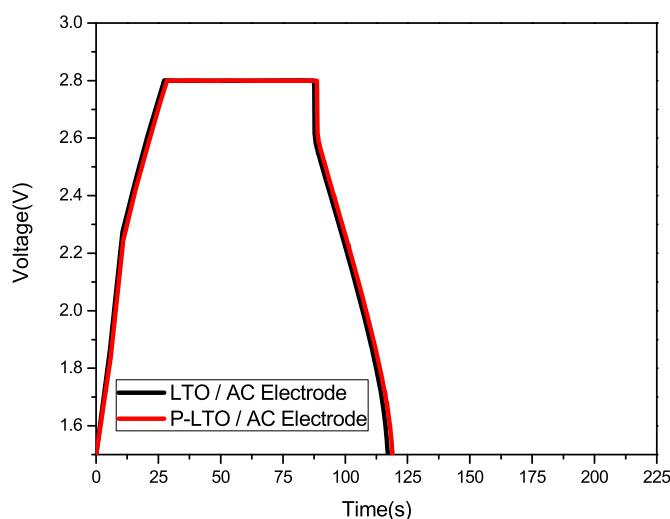


Fig. 4. Initial charge-discharge curves of LTO and P-LTO at a current density of 1 A.

$$R = \frac{V_{\text{charge}} - V_{\text{discharge}}}{2I} \quad (4)$$

' V_{charge} ' is the voltage of the cell at the end charge, ' $V_{\text{discharge}}$ ' is the voltage of the cell at the starting discharge, and ' I ' is the absolute value of charge and discharge current. The IR drop is associated with the electrolyte resistance and the resistance of the electrode materials [15]. In the hybrid supercapacitors, the latter, especially sluggish kinetics of lithium ion at the anode, is main reason for IR drop. Therefore, the IR drop of P-LTO, which has a shorter lithium ion diffusion distance, is slightly smaller than that of granule LTO, indicating the punching could improve the conductivity. The IR drop of P-LTO and granule LTO are 0.178 and 0.189 Ω , respectively. The low internal resistance including IR drop is one of the most important factor in energy storage devices since it can reduce the energy waste used to generate unwanted heat [16]. Although it is not significant difference due to low current density, the P-LTO enables more suitable for high current density because of high electrolyte wetting quality such as speed and continuous supply [17].

Fig. 5 compares the Nyquist plots of P-LTO and granule LTO

based hybrid supercapacitors, indicating the equivalent series resistance (ESR) consisting of electrolyte resistance (R_s), charge transfer resistance (R_{ct}) and Warburg diffusion resistance. We should mention that the R_s in the high frequency is not considered since the same electrolyte was used for hybrid supercapacitors in this paper. As expected, the R_{ct} shows the same tendency with IR drop, as shown in Fig. 4. In middle frequency area, the R_{ct} of the P-LTO is 0.022 Ω , lower than that of granule LTO (0.025 Ω). The R_{ct} measurements indicate that uniform electrolyte distribution and fast lithium ion kinetics can greatly reduce the charge-transfer resistance at the interface between P-LTO and electrolyte [18]. These result indicates that P-LTO can represent an excellent performance not only cycle performances but also fast charge/discharge rates.

To evaluate the rate capability, one of the most important factor, the hybrid supercapacitors were charged and discharged with different current densities from 0.5 to 4 A/g, as shown in Fig. 6. The P-LTO and granule LTO shows the capacity retentions of 98.9 and 98.7%, respectively at a current density of 1 A/g. As the current density increases, the retention of the two hybrid supercapacitors decreases. It can be explained by the reducing utilization of active

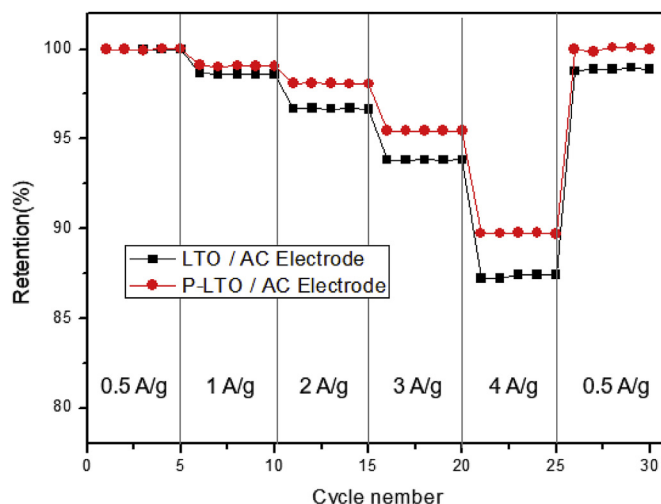


Fig. 6. Rate capabilities of LTO and P-LTO.

materials, resulting from the limited diffusion of lithium ions [19]. However, the two electrodes have different decreasing rates. The retention gap between P-LTO and granule LTO becomes larger with increasing current density. Remarkably, the retention of P-LTO still remains at 90.6% even at a high rate of 4 A/g, much higher than that of granule LTO (87.3%), representing the excellence of P-LTO/AC combination. More importantly, the retention of P-LTO is completely recovered when the current density returned to its initial value, indicating rate reversibility while the capacity recovery of granule LTO is 98.9%. The superior rate-capability of P-LTO can be ascribed by excellent penetration of electrolyte, including lithium salts and solvents, which play important roles in electrochemical performances of hybrid supercapacitors [20]. The P-LTO can considerably decrease the length of the lithium ion diffusion from outside to the deepest part in P-LTO and it would consequently lead to balance out the relatively slow anode and fast cathode [21].

The cycle performances of hybrid supercapacitors using P-LTO and granule LTO as a function of the cycle, as shown in Fig. 7. The super-long cycle life comparable to supercapacitors is another essential capability for hybrid supercapacitors. There is no conspicuous capacity decrease, and it still remains a retention of as high as 99% retention after 14,000 cycles, which proves that P-LTO/AC is a successful combination for outstanding cyclability. The punching structure allows the relaxation of the volume expansion with smooth and rapid lithium ion transport during charge-discharge process [22]. Although granule LTO also exhibits the high cyclability, the relatively insufficient and less uniform electrolyte wetting into granule LTO can be upgraded by punched structure for extraordinary electrochemical performances [6,23]. This is because the locally concentrated electrolyte of granule LTO degrades the long term performances by side reactions between electrode and electrolyte [24].

Fig. 8 shows the Ragone plot of hybrid supercapacitors using P-LTO anode and AC cathode. The energy and power densities can be calculated by the following equations [4]:

$$P = \Delta E \times \frac{I}{m} \quad (5)$$

$$E = P \times t \quad (6)$$

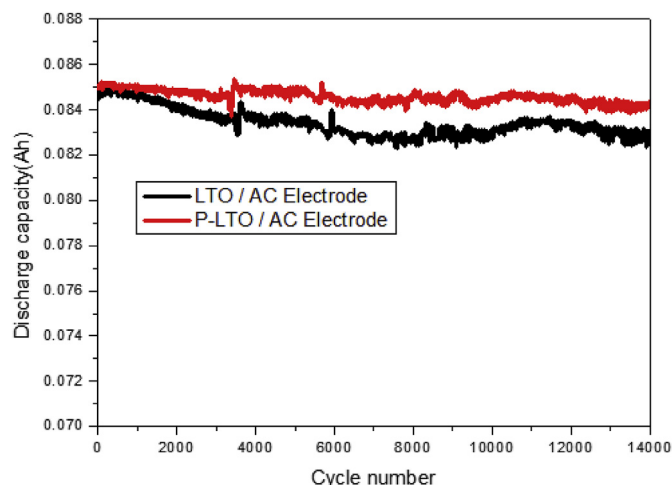


Fig. 7. Cycle performances of LTO and P-LTO.

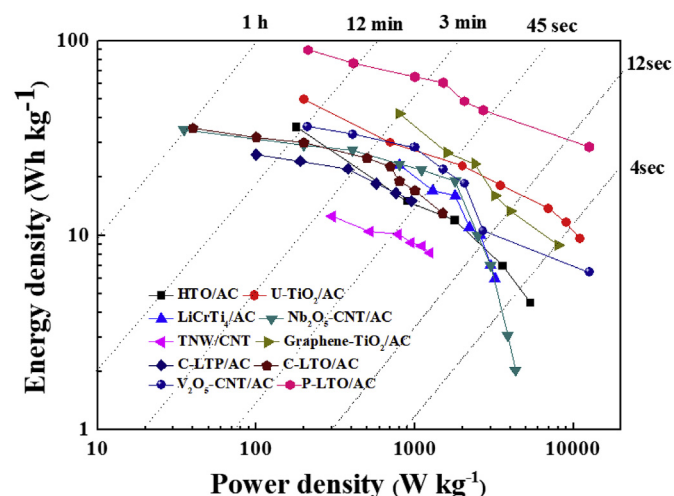


Fig. 8. Ragone plots of P-LTO.

$$\Delta E = \frac{E_{max} + E_{min}}{2} \quad (7)$$

where ' E_{max} ' is the potential at the starting discharge, ' E_{min} ' is the potential at the end discharge, ' I ' is the charge and discharge currents, ' m ' is the mass of active materials including the anode and cathode electrodes, and ' t ' is the discharge time in the hybrid supercapacitor. The energy and power densities of P-LTO anode and AC cathode hybrid supercapacitors ranged from 24.4 to 85.7 Wh kg⁻¹ and from 192.1 to 12,601.5 W kg⁻¹, respectively. These remarkable values also meet the requirement of hybrid electric vehicle (HEV) application. The hybrid supercapacitors using P-LTO/AC show superior energy and power densities compared to other materials such as TiO₂-(reduced graphene oxide)/AC [25], TiO₂-(B) nanowire (TNW)/carbon nanotubes (CNTs) [26], C-Li₄Ti₅O₁₂ (LTO)/AC [27], C-LiTi₂(PO₄)₃ (LTP)/AC [28], V₂O₅-CNT/AC [29], Nb₂O₅-CNT/AC [30], H₂Ti₂O₂₅-AC [4], LiCrTi₄/AC [31], and urchin-like TiO₂/AC [32]. Therefore, we can infer that punched structure of LTO anode is a practical way to improve the energy and power density for hybrid supercapacitors.

4. Conclusion

In summary, we designed P-LTO anode and AC cathode for hybrid supercapacitors and investigated the effect of punching anode on electrochemical performances. The hybrid supercapacitors using P-LTO/AC delivers high electrochemical activity with desirable rate capability and cycle stability. These enhancements can be explained by the following reasons: i) widened effective contact area, ii) P-LTO anode and AC cathode balancing for high electrochemical performances caused by enhanced lithium ion kinetics. iii) thermal stability for high safety. These findings demonstrate that use of punching anode is an effective method for next generation hybrid supercapacitors.

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