



Short communication

A high rate, high capacity and long life (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ hybrid battery–supercapacitor

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ABSTRACT

A hybrid battery–supercapacitor (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ using a Li₄Ti₅O₁₂ anode and a LiMn₂O₄/activated carbon (AC) composite cathode was built. The electrochemical performances of the hybrid battery–supercapacitor (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ were characterized by cyclic voltammograms, electrochemical impedance spectra, rate charge–discharge and cycle performance testing. It is demonstrated that the hybrid battery–supercapacitor has advantages of both the high rate capability from hybrid capacitor AC/Li₄Ti₅O₁₂ and the high capacity from secondary battery LiMn₂O₄/Li₄Ti₅O₁₂. Moreover, the electrochemical measurements also show that the hybrid battery–supercapacitor has good cycle life performance. At 4C rate, the capacity loss in constant current mode is no more than 7.95% after 5000 cycles, and the capacity loss in constant current–constant voltage mode is no more than 4.75% after 2500 cycles.

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1. Introduction

Hybrid electric vehicles (HEVs) can effectively alleviate urban air pollution, reduce greenhouse gas emissions, and save oil [1,2]. But neither secondary batteries (low power density) nor supercapacitors (low energy density) as a single power source for HEVs can meet the need of practical application [3–5]. Therefore, electrochemical energy storage devices with high energy density and high power density are urgently needed. Hybrid battery–supercapacitor is a kind of combination of secondary battery and supercapacitor, and has high energy density as the secondary battery and high power density as the supercapacitor. Thus it is one of the most possible auxiliary power supplies for HEVs. Lam and Louey [6] built an ultra-battery by using a PbO₂ cathode and a composite anode of Pb electrode and activated carbon electrode, which combined an asymmetric capacitor and a lead-acid battery in one unit cell. In contrast with the secondary batteries, the ultra-battery showed higher power density and lower cost. However, it was harmful to the environment. A hybrid battery–supercapacitor using a Li₄Ti₅O₁₂ nanostructured anode and a composite activated carbon LiCoO₂ cathode was built by Pasquier [7], which combined an asymmetric supercapacitor and a Li-ion battery in one unit cell. Compared to the lead-acid ultra-battery, the hybrid battery–supercapacitor showed

higher mass energy density and less pollution, and it is worthy of further study.

Compared with layered LiCoO₂, spinel LiMn₂O₄ has richer natural resources, lower cost, higher safety, easier preparation and non-toxicity [8–12]. Thus LiMn₂O₄ is chosen in our study as the intercalation compound in the composite cathode of the hybrid battery–supercapacitor.

In this paper, we use a composite material from LiMn₂O₄ and activated carbon (AC), as the composite cathode, and then assembled a hybrid battery–supercapacitor device with Li₄Ti₅O₁₂ anode to form the (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ system. It is proved that this new energy storage system has the advantages of high rate, high capacity and long life.

2. Experimental

2.1. Synthesis of anode material

Li₄Ti₅O₁₂ powder was prepared via a solid-state reaction. A stoichiometric mixture of LiOH·H₂O and TiO₂ was dispersed in ethanol and then ball-milled for 5 h. After spraying under a high temperature >120 °C, the precursor was sintered at 1000 °C, and the powder product was further ball-milled again for another 2 h to give the final Li₄Ti₅O₁₂ material.

2.2. Cells assembly and performance evaluation

Cathodes were prepared with LiMn₂O₄ (HLA, China) and AC (GH-6, China). The conductive additives used were colloidal

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Table 1
Formulations of the electrodes tested.

Electrode	Active material	Conductive additives	Binder
15% LMO + AC	LiMn ₂ O ₄ 15% + AC 60%	F-0 12% + SP 6%	LA132 7%
22.5% LMO + AC	LiMn ₂ O ₄ 22.5% + AC 52.5%	F-0 12% + SP 6%	LA132 7%
30% LMO + AC	LiMn ₂ O ₄ 30% + AC 45%	F-0 12% + SP 6%	LA132 7%
LTO	Li ₄ Ti ₅ O ₁₂ 86%	F-0 6% + SP 4%	LA132 4%

graphite (F-0, China) and conductive carbon black (SuperP, TIM-CAL) termed SP hereinafter. The binder used was LA132 (Indigo, China). Anodes were prepared in the same way, using Li₄Ti₅O₁₂ as active material. The electrodes formulations are summarized in Table 1.

The cells were assembled in an argon-filled dry box by pressing a LiMn₂O₄/AC cathode, a Celgard 2400 polypropylene membrane, and a Li₄Ti₅O₁₂ anode. The electrolyte was a 1 M LiPF₆ solution in the mixture of ethylene carbonate, dimethyl carbonate and ethylene methyl carbonate (1:1:1 by weight). The cells were packaged with aluminum-plastic membrane and shaped. The final size of hybrid battery-supercapacitor is 4 mm × 30 mm × 48 mm (thickness × width × length). For comparison, the capacitor AC/Li₄Ti₅O₁₂ and the battery LiMn₂O₄/Li₄Ti₅O₁₂ were also assembled in the same way.

The powders' particle size and particle size distribution were identified by laser particle size analyzer (BT-2003, China). The specific surface area of the powders was carried out on an AUTOSORP ZXF-6 instrument (China) by N₂ adsorption-desorption at 77 K. Rate capability and cycle performance of the hybrid battery-supercapacitor, capacitor and battery were tested on a Repower Battery Tester (China). Cycle performance tests were divided into two modes: constant current mode (CC mode) and constant current-constant voltage mode (CC-CV mode). In CC mode, the hybrid battery-supercapacitors were charge-discharge cycled over a cell-voltage window of between 2.8 V and 1.2 V at a constant current. In CC-CV mode, for each cycle, after resting for 5 min, the hybrid battery-supercapacitors were charged with constant current to 2.8 V and with constant voltage at 2.8 V till charge current declined to 5 mA. Then, they were rested for 5 min. After that, they were discharged to 1.2 V at a constant current. Cyclic voltammograms of the electrodes (LiMn₂O₄, AC and Li₄Ti₅O₁₂) were characterized using a three-electrode cell, the metallic lithium was used as a counter and reference electrodes. The experiment was performed using an Arbin instrument (USA). Electrochemical impedance spectra were investigated by a Solartron 1260/1287 (UK). All the tests were carried out at 20 °C.

3. Results and discussion

3.1. Physical properties of electrode materials

The particle size distribution of LiMn₂O₄, AC and Li₄Ti₅O₁₂ is depicted in Fig. 1. As is seen in this figure, the average particle size of LiMn₂O₄, AC and Li₄Ti₅O₁₂ is 11.47 μm, 12.09 μm and 0.301 μm, respectively. The BET of LiMn₂O₄, AC and Li₄Ti₅O₁₂ is listed in Table 2.

Table 2
The particle size distribution and BET of LiMn₂O₄, AC and Li₄Ti₅O₁₂.

	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	BET (m ² g ⁻¹)
LiMn ₂ O ₄	5.61	11.47	18.33	0.492
AC	3.08	12.09	29.46	582.0
Li ₄ Ti ₅ O ₁₂	0.127	0.301	0.639	10.69

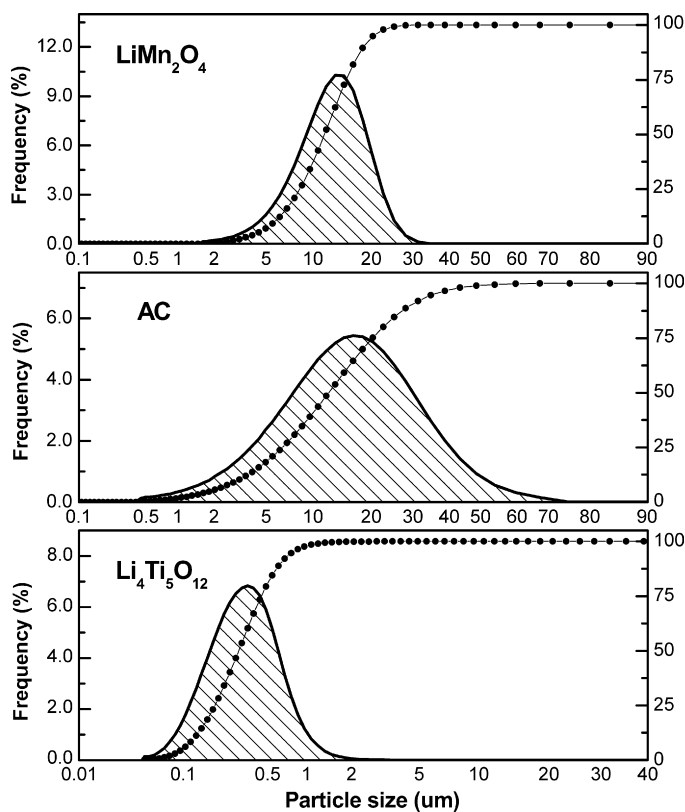


Fig. 1. The particle size distribution of LiMn₂O₄, AC and Li₄Ti₅O₁₂.

3.2. Cyclic voltammetric behavior

The cyclic voltammograms (CVs) of the electrodes, the hybrid battery-supercapacitor (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ and the battery LiMn₂O₄/Li₄Ti₅O₁₂ are shown in Fig. 2. The scan rate of AC electrode is 2 mV s⁻¹ and the others are all 0.2 mV s⁻¹. It is seen from Fig. 2a–c that three materials show different electrochemical behavior. LiMn₂O₄ electrode exhibits oxidation–reduction behavior, i.e., Li-ion insertion–extraction reaction of LiMn₂O₄, and two pairs of redox peaks are located at about 4.0 V and 4.15 V. Li₄Ti₅O₁₂ electrode also exhibits oxidation–reduction behavior, i.e., Li-ion insertion–extraction reaction of Li₄Ti₅O₁₂, and a pair of redox peak is located at about 1.55 V. However, AC electrode exhibits a typical double-layer capacitance behavior, which is due to the process of electric double-layer electrostatic adsorbing–desorbing PF₆⁻¹ in AC. It is obvious that the two cells show different electrochemical behaviors (Fig. 2d and e). LiMn₂O₄/Li₄Ti₅O₁₂ battery system only exhibits oxidation–reduction behavior of the electrodes, i.e., Li-ion insertion–extraction reaction of LiMn₂O₄ and Li₄Ti₅O₁₂ electrodes. (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ hybrid battery-supercapacitor system retains oxidation–reduction behavior of LiMn₂O₄/Li₄Ti₅O₁₂ battery system, i.e., two pairs of redox peaks. Moreover, there is a bigger response current when the (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ hybrid battery-supercapacitor system is in the range of low voltage (curve in a rectangle). It is evident that such response current of electric double-layer is due to the AC component in LiMn₂O₄/AC composite material in the range of low voltage. The above results of CVs illustrate that LiMn₂O₄ and AC components of LiMn₂O₄/AC composite material show electrochemical activity, and bring respective charge storage ability into play in the whole working voltage range.

3.3. Charge–discharge behavior of hybrid battery-supercapacitor

Fig. 3 shows, respectively, a whole charge–discharge process of (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ hybrid battery-supercapacitor,

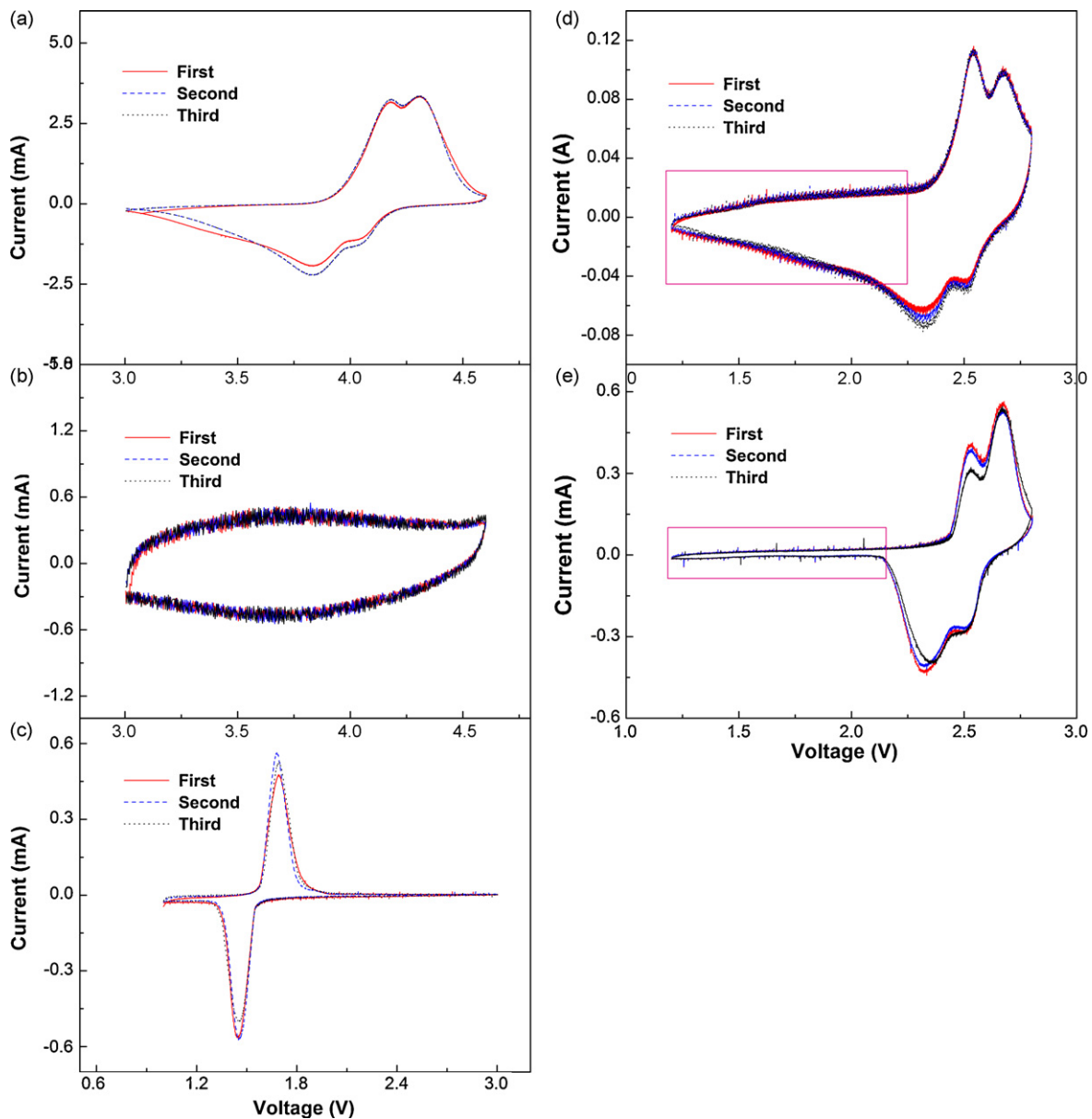


Fig. 2. CVs of the electrodes, the hybrid battery–supercapacitor and the battery: (a) LiMn_2O_4 , (b) AC, (c) $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (d) $(\text{LiMn}_2\text{O}_4 + \text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$, and (e) $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$.

$\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ battery and $\text{AC}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ capacitor. As shown in Fig. 3a, the whole charge–discharge process of $(\text{LiMn}_2\text{O}_4 + \text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$ hybrid battery–supercapacitor does not exhibit obvious voltage plateau. Compared with Fig. 3b and c, there is an obvious difference. $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ battery exhibits the process of Li-ion extraction–insertion in LiMn_2O_4 and Li-ion insertion–extraction in $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which presents typical Faradaic energy storage. $\text{AC}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ hybrid capacitor exhibits the process of electric double-layer electrostatic adsorbing–desorbing PF_6^{-1} in AC and Li-ion insertion–extraction in $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which presents energy storage of electric double-layer electrostatic adsorption. $(\text{LiMn}_2\text{O}_4 + \text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$ hybrid battery–supercapacitor is the combination of Faradaic energy storage and electric double-layer energy storage. It is worth noting that steps A–B and C–D represent typical electric double-layer energy storage.

A comparison of the results between charge–discharge process curve (Fig. 3a) and CVs curve (Fig. 2d) of $(\text{LiMn}_2\text{O}_4 + \text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$ hybrid battery–supercapacitor shows steps A–B and C–D in charge–discharge curve are corresponding to the left part (curves

inside the rectangle) in the CVs curve and other steps are corresponding to the right part (curves outside of the rectangle). The results indicate that the charge–discharge cycle curve of $(\text{LiMn}_2\text{O}_4 + \text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$ hybrid battery–supercapacitor is consistent with the CVs curve. These facts illustrate that in the whole working voltage range the hybrid battery–supercapacitor $(\text{LiMn}_2\text{O}_4 + \text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows two modes of energy storage and presents two electrochemical performances mainly due to the presence of small amount of LiMn_2O_4 in the $\text{LiMn}_2\text{O}_4/\text{AC}$ composite cathode. It is proven that the hybrid battery–supercapacitor $(\text{LiMn}_2\text{O}_4 + \text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$ system is composed of the capacitor system and the secondary battery system.

3.4. Electrochemical impedance spectra (EIS) of hybrid battery–supercapacitor

Fig. 4 shows EIS of hybrid battery–supercapacitor (22.5% $\text{LiMn}_2\text{O}_4 + \text{AC})/\text{Li}_4\text{Ti}_5\text{O}_{12}$ at various potentials. The a.c. amplitude is 10 mV, and frequency range is 100 kHz to 0.1 Hz. It can be seen that

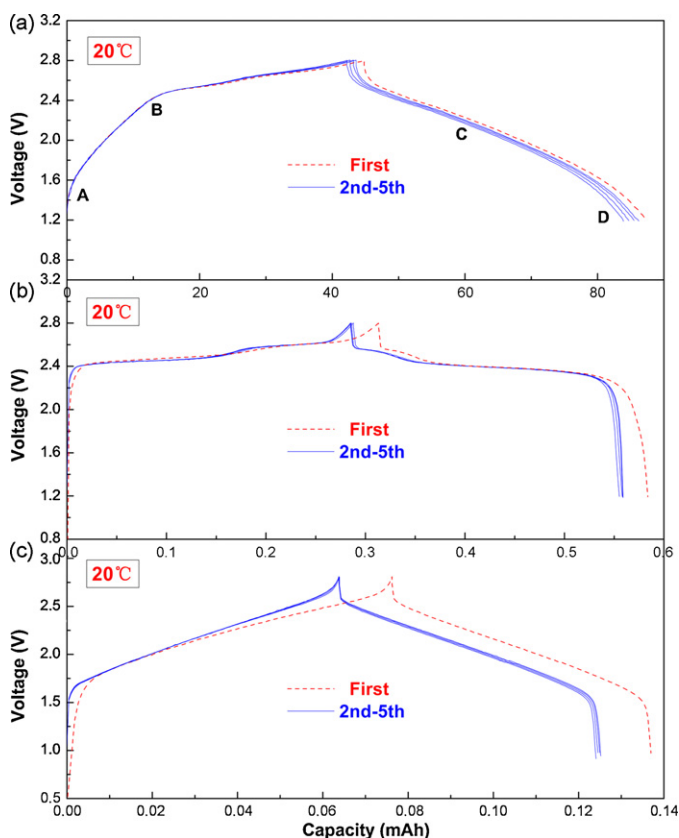


Fig. 3. Current charge-discharge cycle of the hybrid battery-supercapacitor ($\text{LiMn}_2\text{O}_4 + \text{AC}$)/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a), the battery LiMn_2O_4 / $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (b), and the capacitor $\text{AC}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ (c).

Nyquist plot does not change with potential, which is composed of two parts: an almost vertically straight line & semicircle in the high frequency range and a slash in the low frequency range. The equivalent circuit is made of a connector's inductance (L), an electrolyte resistance (R_{el}), a charge-transfer resistance (R_{ct}), a double-layer

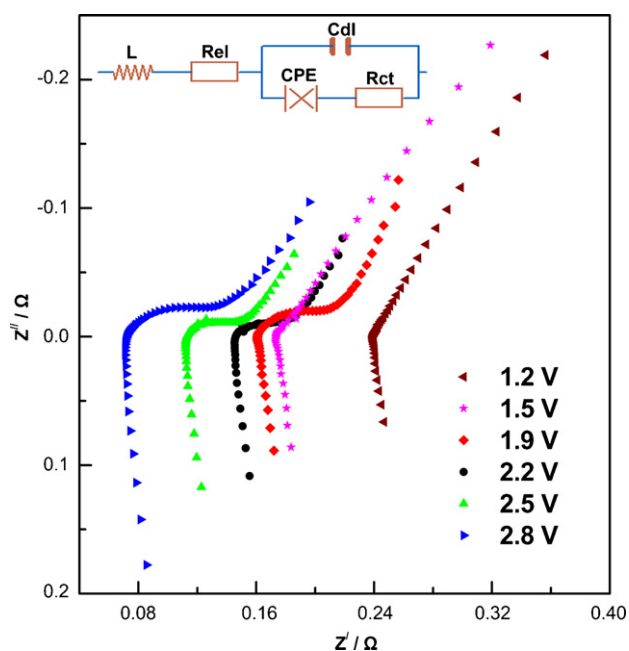


Fig. 4. EIS of the hybrid battery-supercapacitor at various potentials.

Table 3

Energy densities of hybrid battery-supercapacitors at 4C rate.

Type	Current (mA)	Energy density		
		Wh kg^{-1}	Wh L^{-1}	
CC mode	(15% LMO + AC)/LTO	200	9.81	15.68
	(22.5% LMO + AC)/LTO	220	10.39	17.14
	(30% LMO + AC)/LTO	240	11.06	18.24
CC-CV mode	(15% LMO + AC)/LTO	200	12.84	21.18
	(22.5% LMO + AC)/LTO	220	15.00	24.74
	(30% LMO + AC)/LTO	240	16.47	27.17

capacitance (C_{dl}), and a constant phase element (CPE). CPE reflects capacitance characteristics of the hybrid battery-supercapacitor. With the increase of potential (from 1.2 V to 2.8 V), R_{el} decreases (from 0.241Ω to 0.07359Ω), and n of CPE also decreases (from 0.6708 to 0.4865). These results demonstrate that with the increase of potential the capacitance characteristics becomes weaker while the battery characteristics becomes stronger, indicating that energy storage process in the hybrid battery-supercapacitor is gradually transferred from energy storage of electric double-layer electrostatic adsorption to Faradaic energy storage.

3.5. Energy density of hybrid battery-supercapacitor

Table 3 shows the results of the energy densities of the hybrid battery-supercapacitors in CC and CC-CV modes. In two modes, the mass and volume energy densities of ($\text{LiMn}_2\text{O}_4 + \text{AC}$)/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ hybrid battery-supercapacitors with various LiMn_2O_4 contents all exceed 9.81 Wh kg^{-1} and 15.68 Wh L^{-1} , respectively. The energy density of hybrid battery-supercapacitor is enhanced when the content of LiMn_2O_4 is added in composite cathode. When the content of LiMn_2O_4 in composite cathode is 30 wt% in CC-CV mode, the mass and volume energy densities of ($\text{LiMn}_2\text{O}_4 + \text{AC}$)/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ hybrid battery-supercapacitor reach 16.47 Wh kg^{-1} and 27.17 Wh L^{-1} , respectively. These results demonstrate ($\text{LiMn}_2\text{O}_4 + \text{AC}$)/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ hybrid battery-supercapacitors have high energy density at 4C rate.

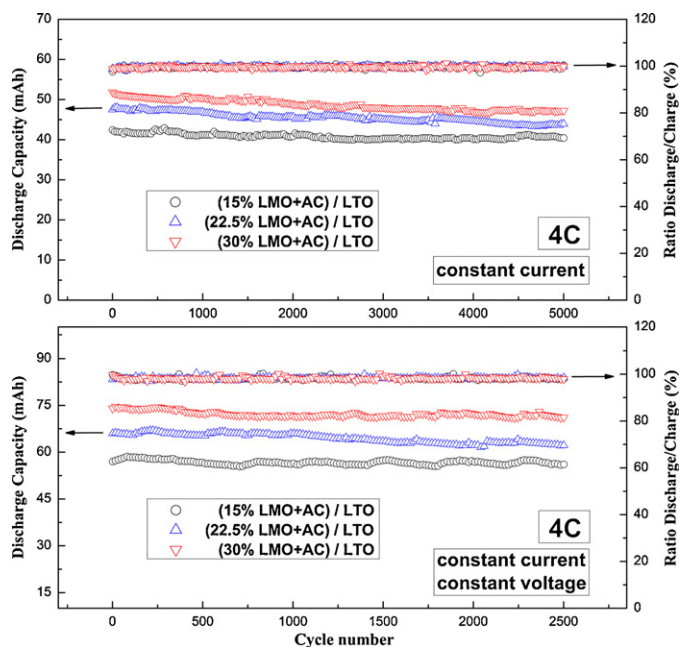


Fig. 5. Discharge capacity and discharge/charge ratio vs. cycle number for hybrid battery-supercapacitors at 4C rate.

3.6. Cycle life performance of hybrid battery–supercapacitor

The results for cycle life of the hybrid battery–supercapacitors at 4C rate are shown in Fig. 5. (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ hybrid battery–supercapacitors in two modes provide high coulombic efficiencies closed to 100%. In CC mode, when the content of LiMn₂O₄ in composite cathode is 15 wt%, 22.5 wt% and 30 wt%, after 5000 cycles the capacity loss of (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ hybrid battery–supercapacitor is 4.72%, 7.19% and 7.95%, respectively. Clearly, all the value is no more than 7.95%. However, if in CC–CV mode, after 2500 cycles the capacity loss will be 1.58%, 4.75% and 3.92%, respectively, and noticeably, all the value is no more than 4.75%. The results show that (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ hybrid battery–supercapacitors have good cycle life performance at high rate.

4. Conclusion

The hybrid battery–supercapacitor (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ system is composed of the capacitor system and the secondary battery system, and has the advantages of high rate, high capacity and long life. At 4C rate, when the content of LiMn₂O₄ in composite cathode is 30 wt% in CC–CV mode, the mass and volume energy den-

sities of (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ hybrid battery–supercapacitor reach 16.47 Wh kg⁻¹ and 27.17 Wh L⁻¹, respectively. The capacity loss of (LiMn₂O₄ + AC)/Li₄Ti₅O₁₂ hybrid battery–supercapacitors in CC mode is no more than 7.95% after 5000 cycles, and the capacity loss in CC–CV mode is no more than 4.75% after 2500 cycles.

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