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Polarity-switchable symmetric graphite batteries with high energy and high power densities

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Abstract:

Multifunctional batteries with enhanced safety performance have received considerable attention for their applications at the extreme conditions. However, few batteries can endure the mix-up of battery polarity during charging, a common wrong operation of rechargeable batteries. Herein for the first time, we propose a polarity-switchable battery based on dual-intercalation chemistry of graphite. The unique redox-amphoteric intercalation feature of graphite allows a reversible switch of graphite between anode and cathode, thus enabling polarity-switchable symmetric graphite batteries. The large potential gap between anion and cation intercalation delivers a high midpoint device voltage ($\approx$ average voltage) of ~ 4.5 V. Further, both the graphite anode and cathode are kinetically activated during the polarity switch. Consequently, our polarity-switchable symmetric graphite batteries exhibit a remarkable cycling stability (96% capacity retention after 500 cycles), a high power density of 8.66 kW/kg and a high energy density of 227 Wh/kg (calculated based on the total weight of active materials in both anode and cathode), which are superior to other symmetric batteries and recently reported dual-graphite or dual-carbon batteries. Our work will inspire

the development of new multifunctional energy storage devices based on novel materials and electrolyte systems.

Multifunctional energy storage devices with high energy density yet low cost are arousing tremendous interest for scalable and sustainable application in smart consumer products.^[1] Various functions including self-healing,^[2] self-heating,^[3] thermo-protection,^[4] and photo-rechargeability^[5] have been incorporated into rechargeable batteries to enhance safety property and/or battery performance under specific conditions (electrode damage, low temperature, overheat and solar energy). Although significant progress has been achieved, few batteries can tolerate the mix-up of battery polarity during charging. That is, only one charging direction is allowed. Accidentally charging batteries in the wrong direction will cause severe structural damage even explosion and fire, raising safety concerns on the tolerance of high-energy batteries against wrong operation. Alternatively, designing rechargeable batteries with switchable polarity (function in two directions) via different energy storage mechanism may provide an effective solution.

Symmetric batteries, which utilize the same active material as both anode and cathode, have recently become a research focus owing to largely simplified fabrication process and reduced manufacturing cost.^[6] One intriguing merit of symmetric batteries lies at the ability of charging/discharging in both directions (switchable polarity). However, limited efforts have been taken into this aspect thus far. On the other hand, the current symmetric batteries heavily rely on cationic redox reactions of lithium or sodium-based transition metal oxide compounds like LiVPO_4F ,^[7] $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$,^[8] $\text{Na}_{0.66}\text{Ni}_{0.17}\text{Co}_{0.17}\text{Ti}_{0.66}\text{O}_2$ ^[9] and $\text{Na}_2\text{VTi}(\text{PO}_4)_3$ ^[10], which restrict the further enhancement of average device voltage (1.2-3.1 V) and energy density (40-139 Wh/kg) (Table S1 in Supporting Information). Therefore, it is highly appealing to develop new symmetric batteries with switchable polarity, higher energy density and lower cost.

Herein we report a polarity-switchable battery based on symmetric graphite electrodes, where a dual-intercalation mechanism is involved. During charging, anions (PF_6^-) and cations (Li^+) in the electrolyte intercalate into graphite cathode and anode, respectively (**Scheme 1**). While in the discharging process, both ions diffuse back into the electrolyte. Once switching the battery polarity, the graphite electrode allows counter ions' intercalation due to the unique redox-amphoteric intercalation feature of graphitic carbon.^[11] As the result, our symmetric graphite batteries based on inexpensive bulk graphite exhibit impressive polarity switchability and stable cycling performance. More interestingly, a switch-induced activation of anode and cathode is observed, which gives rise to enhanced electrochemical kinetics. A high midpoint device voltage of ~ 4.5 V, a high energy density of 227 Wh/kg and a peak power density of 8.6 kW/kg are achieved for the switchable symmetric graphite batteries, which surpass other symmetric batteries^[7-10] and recently reported dual-graphite (carbon) batteries.^[12]

To prepare the graphite electrodes, commercial graphite powders with limited surface area ($5\text{-}8\text{ m}^2/\text{g}$, Figure S1) and large size ($10\text{-}60\text{ }\mu\text{m}$, Figure S2) were investigated as the active material. Considering the large volume variation over 130%^[11a] during anion intercalation into graphite, a strong aqueous binder, alginate sodium, was used to enhance the graphite electrode integrity. Instead of using Al and Cu current collectors in commercial Li-ion batteries, stainless steel foil was applied here due to its wide electrochemical potential window up to 6 V (vs Li/Li^+ , Figure S3). The electrolyte is 2M LiPF_6 in ethyl methyl carbonate (EMC) with 3 wt% vinylene carbonate (VC), which facilitates the formation of solid-electrolyte interphase (SEI) on anode.^[13]

The electrochemical switchability of graphite anode was first investigated in half cells (Li as the counter electrode) by adjusting potential ranges sequentially (0.01-1.5, 3-5 and 0.01-1.5 V vs Li/Li^+). Note that the “switch” in half cells is defined as changing the potential range from one to another; while the “switch” in full cells is reversing the battery polarity. In the anode range (0.01-1.5 V), the graphite electrode shows a limited capacity of 100-140 mAh/g

at 0.1 A/g (**Figure 1a, d**), which is far below the theoretical value of 372 mAh/g and this may suffer from the SEI formation problem. Analyzing the charge-discharge curves (**Figure 1a**), no reductive decomposition plateau of VC was observed in the potential range of 1.05-1.4 V (vs Li/Li⁺)^[14], implying no substantial SEI formed. The scanning electron microscope (SEM) image of graphite anode after 20 cycles (**Figure 1f and S4b**) further confirmed that only limited particle-like SEI were generated on the graphite surface. This result suggests that graphite anode was not fully utilized in 2M LiPF₆ electrolyte with 3 wt% VC because of the insufficient SEI.

Shifting to the cathode range (3-5 V vs Li/Li⁺), the graphite electrode experienced a conditioning process to reach a reversible capacity of 84 mAh/g (**Figure 1b, d**). The abnormally high charge capacities at the first several cycles can be mainly assigned to the VC oxidation,^[15] which was frequently observed in VC-containing electrolyte for dual-ion batteries and accompanied with initial low Coulombic efficiencies (CEs).^[13a] Nevertheless, the discharge curve manifested three distinct anion (PF₆⁻) deintercalation stages at 4.1-4.45, 4.45-4.82 and 4.82-5 V (vs Li/Li⁺) (**Figure 1b**). At the same time, a high midpoint voltage of ~4.5 V was achieved, which is much higher than those of conventional transition metal oxide cathodes for Li-ion batteries and symmetric batteries. In addition, neither obvious SEI nor VC oxidation product was found on graphite cathode (**Figure 1g and S4c**).

Switching back to the anode range, the reversible capacity of graphite anode was largely enhanced to ~365 mAh/g (**Figure 1c, d**), which is 2.62 times greater than 140 mAh/g of unswitched graphite anode. Simultaneously, two peaks corresponding to LiC₆ and LiC₁₂ appeared on X-ray diffraction (XRD) patterns of lithiated graphite anode (**Figure S5**). A typical reductive decomposition plateau of VC was noticed on the discharge curve of the 41st cycle (**Figure 1c**), implying considerable SEI formation by VC. The SEM image further evidenced the uniform and dense particle-like SEI on switched graphite anode (**Figure 1h and S4d**). The typical Li⁺ intercalation plateaus of graphite were also noticeable below 0.2 V

(Li/Li⁺). Besides higher capacity, the switched graphite anode also showed faster electrochemical kinetics. The electrochemical impedance spectra (EIS) in Figure 1e revealed that the switched graphite anode had a smaller charge transfer resistance (the semicircle in high-medium frequency region) of ~30 Ω , in contrast to 300 Ω of unswitched graphite anode. All these results suggest that the switch process induced dense SEI formation on graphite anode, activating graphite for higher capacity and faster kinetics.

The electrochemical switchability of graphite cathode was next examined under similar condition except adjusting potential ranges in a different sequence (3-5, 0.01-1.5 and 3-5 V vs Li/Li⁺). The graphite electrode delivered stable capacities of 82, 370 and 87 mAh/g at each range (**Figure 2a-d**), and similar VC oxidation and VC reduction-induced SEI formation plateaus were observed in cathode and anode ranges (Figure 2a-c). Different from the obvious capacity increase of graphite anode during the switch process (Figure 1d), the graphite cathode only displayed a ~6% capacity enhancement (87 vs 82 mAh/g) after switch (Figure 2d). Regarding the EIS in Figure 2e, the switched graphite cathode exhibited smaller charge transfer resistance (59 Ω vs 70 Ω) and better mass transfer (the sloping line in low frequency region) than the unswitched graphite cathode. Thereby, the graphite cathode was also activated during the switch process.

Benefiting from the fact that graphite electrode can reversibly switch between anode and cathode in 2M LiPF₆ electrolyte with 3 wt% VC (Figure 1a and 2a), symmetric graphite batteries with switchable polarity were consequently constructed in a cathode/anode weight ratio of 1/1. The high potential gap between anion and cation intercalation leads to a high midpoint device voltage ($\approx$ average voltage) of ~4.5 V, which is the highest value among all the reported symmetric batteries (Table S1). The polarity switchability of the symmetric graphite batteries was first investigated by the galvanostatic charge-discharge test at 0.1 A/g (**Figure 3a**). The pristine battery showed a stable discharge capacity of 83 mAh/g after 20 cycles. Afterwards, the battery was switched in polarity and tested under the same condition.

An enhanced discharge capacity of 90 mAh/g was achieved after the first switch and remained quite stable after the second and third switch with an increased CE. The capacity enhancement can be attributed to the activation effect of graphite anode and cathode during the switch process as we observed in half cells. Figure 3b illustrates that our symmetric graphite battery can reversibly switch the battery polarity and power a high-voltage (2.4-4.6 V) white light-emitting diode (LED) in both directions. No structural damage was observed during the switch, thus achieving much better tolerance against polarity mix-up over conventional unswitchable batteries. Abnormally high charge capacities were observed at the first cycle and initial cycles (21st, 41st and 61st) of each switch, and the charge curves featured with two apparent plateaus at -1.4 V and >4V (Figure 3c), which can be assigned to VC reduction-induced SEI formation, VC oxidation and Li⁺/PF₆⁻ dual-ion intercalation. From the 22th cycle, the charge-discharge curves of symmetric graphite batteries well overlapped with each other, showing high cycling stability during polarity switch (Figure 3d).

The polarity-switchable symmetric graphite batteries also show a remarkable rate capability. The switched symmetric graphite batteries possess some capacitor-like high power features and are insensitive to the current rates (**Figure 4a**). No distinct capacity fading was observed (91.4→89.4 mAh/g) when the current density increased from 0.2 to 1 A/g (Figure 4b). Even at a large charge rate of 2A/g, a capacity of 82 mAh/g could still be maintained, which is much higher than 53.4 mAh/g of the unswitched symmetric graphite batteries (Figure S6). In addition to the high rate capability, the polarity-switchable symmetric graphite batteries exhibited outstanding cycling performance. After 500 cycles under 0.5 A/g, the capacity retention was up to 96% accompanied by a high average CE of 95.1% (Figure 4c and S7), representing high reversibility of the dual-intercalation chemistry.

In order to further push forward the performance of our symmetric graphite batteries, a wider voltage window of 3-5.2 V was applied. As shown in Figure 4d, high reversible capacities of 100.2, 100.5, 100, 99.4, 94.4, 90.1 and 85.6 mAh/g were obtained at 0.2, 0.4, 0.8,

1, 2, 3 and 4 A/g, respectively. Compared with the recently reported dual-graphite^[12a, 12b, 12d, 12f] or dual-carbon batteries^[12c, 12e, 12j], our switchable symmetric graphite batteries presented the superior rate capability (Figure 4e), which is associated with the fast intercalation kinetics of graphite electrodes activated by polarity switch. The power density of our symmetric graphite batteries are estimated to be 0.45-8.66 kW/kg (0.45-4.36 kW/kg in 3-5 V) while maintaining the energy density in the range of 185-227 Wh/kg (179-205 Wh/kg in 3-5 V, Figure 4f, Table S2 and S3), surpassing all the thus far reported symmetric batteries^[7-10] and dual-graphite (carbon) batteries^[12].

In summary, we have demonstrated the first polarity-switchable battery based on symmetric graphite electrodes, where dual-intercalation chemistry of graphite is involved. The resultant symmetric graphite batteries can be charged/discharged in both directions, thus exhibiting high safety properties and tolerance against polarity mix-up. During the polarity switch, the graphite electrodes were activated in 2M LiPF₆ electrolyte with 3 wt% VC, leading to higher capacity and faster electrochemical kinetics. VC reduction-induced SEI formation and VC oxidation were observed as well. As a consequence, our polarity-switchable symmetric graphite batteries showed capacitor-like high power density and maintained high energy density, superior to other reported symmetric batteries and dual-graphite (carbon) batteries. Our strategy for symmetric graphite batteries can be readily extended to other carbon materials and new electrolyte systems to construct multifunctional energy storage devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Scheme 1. Working principle of polarity-switchable symmetric graphite batteries: switchable anion and cation intercalation into graphite electrodes.

Figure 1. The switchability of graphite anode in half cells. (a-c) Charge-discharge curves and (d) cycling performance of graphite electrode in different potential ranges (0.01-1.5 V, 3-5 V and 0.01-1.5 V vs Li/Li⁺) at 0.1 A/g; (e) EIS of graphite electrode at different cycle; (f-h) SEM images of cycled graphite electrodes.

Figure 2. The switchability of graphite cathode in half cells. (a-c) Charge-discharge profiles and (d) cycling performance of graphite electrode in different potential ranges (3-5 V, 0.01-1.5 V and 3-5 V vs Li/Li⁺) at 0.1 A/g; (e) EIS of graphite electrode at different cycle.

Figure 3. Polarity-switchability of symmetric graphite batteries. (a) Cycling stability after each polarity switch at 0.1 A/g; (b) powering a white LED after each switch; (c, d) the charge-discharge curves at different cycle.

Figure 4. Electrochemical performance of polarity-switchable symmetric graphite batteries. (a) The charge-discharge curves and (b) rate performance of symmetric graphite batteries with and without polarity switch. (c) cycling performance at 0.5 A/g. (d) charge-discharge curves of polarity-switchable symmetric graphite batteries at various current rates in a voltage window of 3-5.2 V; (e) rate performance comparison and (f) Ragone plots of our polarity-switchable symmetric graphite batteries. The energy density and power density were calculated based on the total weight of active materials in both anode and cathode.

The first polarity-switchable battery based on dual-intercalation chemistry of graphite is proposed and demonstrated. During the polarity switch, the symmetric graphite battery shows no structural damage, exhibiting excellent tolerance against polarity mix-up. Owing to an activation effect of graphite electrodes, both high energy and high power densities are achieved in the switchable symmetric graphite batteries.

Polarity-switchable batteries

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Polarity-switchable symmetric graphite batteries with high energy and high power densities