High Performance Lithium-ion and Lithium-Sulfur Batteries using Prelithiated Phosphorus/Carbon Composite Anode

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High Performance Lithium-ion and Lithium-Sulfur Batteries using Prelithiated Phosphorus/Carbon Composite Anode

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Abstract

Controlled chemical prelithiation of high capacity phosphorous/carbon (P/C) composite anode has been applied to develop advanced lithium-ion batteries (LIBs). The initial coulombic efficiency (CE) of P/C is significantly improved (up to 93% for fully-prelithiated P/C) owing to the formation of an artificial solid electrolyte interface (SEI) layer, which is characterized by SEM, Raman and XPS analyses. It ensures the application of P/C anode in real battery assembly. A partly-prelithiated P/C anode prepared by 20 sec prelithiation treatment is paired with a LiCoO2 (LCO) cathode. The full cell delivers a highly reversible capacity of ~ 104 mAh g-1LCO at 1C rate and retains a CE close to 100% over 2000 cycles. Moreover, a fully-prelithiated P/C anode prepared by 10 min prelithiation treatment is paired with a high-capacity Li-free sulfur/carbon (S/C) cathode. This newly configured full cell delivers a good rate and cycling performance and a high energy density of 358 Wh kg-1.

Keywords

Lithium-ion batteries, Prelithiation, Initial coulombic efficiency, Phosphorous, Sulfur

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are widely used for portable electronics and exhibit great potential for electric vehicles and stationary energy storages[1, 2]. To fulfill the growing market demand, efforts have been devoted to developing advanced or beyond LIBs with improved energy densities and reduced cost[3]. One effective way is to replace the conventional graphite anode (372 mAh g^{-1}) with materials that have higher specific capacities[4]. Phosphorus (P)[5], especially in its red allotropic form, is a promising alternative because of its high theoretical capacity (2596 mAh g^{-1}), chemically stable nature and abundant reserve[6, 7]. Nevertheless, its insulating nature ($<10^{-14}$ S cm^{-1}) and drastic volume change (~490%) during charge/discharge leads to a low rate capability and poor cycle life[8]. To address these problems, various carbon materials have been introduced to simultaneously provide a conducting pathway and alleviate the volume expansion[[9], [10], [11], [12]]. Both the specific capacity and cyclability of these P/C composites were dramatically improved relative to those of pristine red P. Despite this progress, the initial coulombic efficiency (CE) of these P/C composites is typically in the range of 40% ~ 80% owing to the formation of the solid electrolyte interphase (SEI) layer[6, 13], far below that of commercial graphite anode (>90%)[14, 15]. For half cells widely used in academic studies, which usually have a greatly excessive amount of active Li ions from Li metal counter electrode, the low initial CE doesn't cause any detrimental effect. However, for full cells with limited Li source, since the Li-free P/C anode needs to be coupled with Li-containing cathodes, usually lithium metal oxides that have low specific capacity, a substantial amount of active Li ions from the cathode are consumed and permanently trapped on anode surface during the first charge, consequently, the available capacity is significantly reduced[16, 17].

Prelithiation is an effective way to mitigate such drawback[18]. Many prelithiation attempts have been made so far[16, 19], such as anode prelithiation[[20], [21], [22]], cathode over-lithiation[23], and sacrificial electrode or electrolyte additives[24, 25]. In particular, the anode prelithiation could not only reduce the loss of active Li ions in the first charge but also enable the pairing with Li-free cathode materials that have high capacities[26]. We have recently reported that lithium-biphenyl (Li-Bp)/tetrahydrofuran (THF) solution is an effective reagent for the chemical prelithiation of various anode materials including P[27]. In this work, we demonstrate the practicability of using this prelithiation reagent (Li-Bp/THF) in developing advanced full LIBs with P/C anode. The prelithiated P/C anodes with certain degree of prelithiation (DOPL) were controllably prepared and separately coupled with Li-containing $LiCoO_2$ cathode and Li-free sulfur/carbon (S/C) cathode to form full cells. High capacity and long cycle life were demonstrated in both cases.

2. Experimental section

2.1. Synthesis of P/C and S/C composites

The P/C composite (40 wt.% P) and mesoporous carbon were synthesized as reported in our previous paper[28]. The S/C composite was prepared by a similar strategy except using a different heat treatment procedure. 150 mg of as-prepared mesoporous carbon was put into a glass tube (A). A smaller glass tube (B) filled with 350 mg of sulfur powder was inserted into the glass tube A. The glass tube A was then sealed under vacuum, heated to 550 °C with a heating rate of 5 °C/min and held at 550 °C for 12 h. The S/C composite was obtained after the vessel naturally cooled to room temperature without any further treatment. The scanning electron microscope (SEM, Hitachi-S4800) image, EDX elemental mapping and thermogravimetric analysis (TGA, TA SDT650) curve of the homemade S/C composite are shown in Fig. S1. The sulfur content in S/C composite was determined to be 64.3 wt.% according to TGA analysis.

2.2. Prelithiated P/C anode

The pristine P/C electrode was prepared by coating a slurry containing the homemade P/C composite (75 wt.%), super C65 conductive agent (10 wt.%), and carboxymethyl cellulose (CMC) binder (15 wt.%) on a carbon-coated Cu foil substrate (MTI corporation). The electrode was then dried under vacuum at 60 °C overnight. The mass loading of P/C composite was 0.8 ~ 1.1 mg cm^{-2}. The prelithiated P/C electrodes were prepared by immersing the pristine P/C electrode into 1 M lithium-biphenyl/tetrahydrofuran (Li-Bp/THF) solution for treatment. The degree of prelithiation (DOPL) was controlled by the treatment duration. To prevent further reaction, the prelithiated electrodes were immediately washed with anhydrous THF several times to remove the residual Li-Bp and then dried under vacuum. All operations were performed in an Ar-filled glovebox.

2.3. $LiCoO_2$ cathode

The $LiCoO_2$ (LCO) electrode was prepared by coating a slurry containing a commercial $LiCoO_2$ powder (90 wt.%), super C65 conductive agent (5 wt.%), and polyvinylidene fluoride (PVDF) binder (5 wt.%) on a carbon-coated Al foil substrate (MTI corporation). The electrode was then dried under vacuum at 60 °C overnight. The mass loading of LCO was 3.0 ~ 4.0 mg/cm^2.

2.4. S/C cathode

The S/C electrode was prepared by coating a slurry containing the homemade S/C composite (70 wt.%), super C65 conductive agent (15 wt.%), and PVDF binder (15 wt.%) on a carbon-coated Al foil substrate. The electrode was then dried under vacuum at 60 °C overnight. The mass loading of S/C composite was ~ 1.0 mg/cm^2.

2.5. Electrochemical Test

The pristine and prelithiated P/C electrodes (1/2 inch) were measured using a half cell configuration with Li metal as the counter electrode. The electrolyte was 1 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v, BASF) with 10 wt.% fluoroethylene carbonate (FEC) and 2 wt.% vinylene carbonate (VC) as additives unless otherwise specified. The amount of electrolyte used in each cell was ca. 60 µl. The separator was Celgard 2325. The galvanostatic charge/discharge tests were performed between 0.01 V and 2.5 V.

The LCO vs. P/C LIB and LCO vs. partly-prelithiated P/C LIB were assembled using the same electrolyte (also 60 µl for each cell) and separator as P/C half cell. The size of the anode (1/2 inch) is slightly larger than that of the cathode (7/16 inch) in order to facilitate alignment of the two electrodes. The total mass ratio of P/C to LCO is ca. 1:3.3 (The area capacity ratio of the anode to the cathode is ca. 1.1:1). The galvanostatic charge/discharge tests were performed between 2.1 V and 3.3 V.

The S/P LIB was assembled using the fully-prelithiated P/C as the anode (1/2 inch) and the S/C as the cathode (7/16 inch). The total mass ratio of P/C to S/C is ca. 1.3:1. The electrolyte was 1 M Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:1 v/v, BASF) with 0.4 M lithium nitrate ($LiNO_3$) as additive. The amount of electrolyte used in each cell was ca. 30 µl. The separator was also Celgard 2325. The galvanostatic charge/discharge tests were performed between 0.7 V and 2.0 V.

All galvanostatic charge-discharge curves were measured using a battery tester (Arbin Instruments) at room temperature.

2.6. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex600 with Cu Kα radiation. The prelithiated P/C powder synthesized in glovebox was sealed in a quartz sample holder with Kapton tape in order to avoid exposure to air and moisture. Raman measurements were carried out using an XploRA PLUS (Horiba Scientific) with a 532 nm laser. All electrodes were sealed in a quartz cell during Raman analysis. X-ray photoelectron spectroscopy (XPS) analysis were performed using an ESCALAB250Xi (Thermo Fisher Scientific) spectrometer. The electrodes were taped on a sample holder inside glovebox, sealed in an airtight box, and quickly transferred into XPS chamber.

3. Results and discussion

The pristine P/C electrode exhibits a large irreversible capacity in the first formation cycle (Fig. 1c), and the initial CE is only 74% (Fig. 1d). A series of prelithiated P/C electrodes were obtained by immersing the pristine P/C electrode into 1 M Li-Bp/THF solution for various durations. Fig. 1a and 1b show the voltage profiles of these prelithiated P/C electrodes for the 1st and 2nd cycle, respectively. Li metal was used as the counter electrode. The corresponding capacities are summarized in Fig. 1c, in comparison with those of the pristine P/C electrode. With increasing treatment time, the initial delithiation capacities of these prelithiated P/C electrodes gradually increased until reaching a maximum constant value of ~ 900 mAh $g^{-1}_{P/C}$ (~2250 mAh g^{-1}_{P}), corresponding to 87% of the theoretical capacity of P. While the capacities of the subsequent cycles (1st lithiation, 2nd delithiation and 2nd lithiation) were all close to those of the pristine P/C electrode, suggesting no detachment of active material from current collector substrate due to volume increase. These results were seen even after a long immersion period of 60 min. In addition, as shown in Fig. 1e, the prelithiated P/C shows an excellent rate capability as current density increased. It delivers a high reversible capacity of around 880 mAh $g^{-1}_{P/C}$ at 2 A g^{-1}. The specific capacity returns to 1100 mAh $g^{-1}_{P/C}$ when the current density was restored to 0.1 A g^{-1}. After the rate tests, the prelithiated P/C continued to be cycled at 0.1 A g^{-1} over 240 cycles (over seven months), during which the electrode exhibits an excellent cycling stability with a capacity beyond 950 mAh $g^{-1}_{P/C}$.

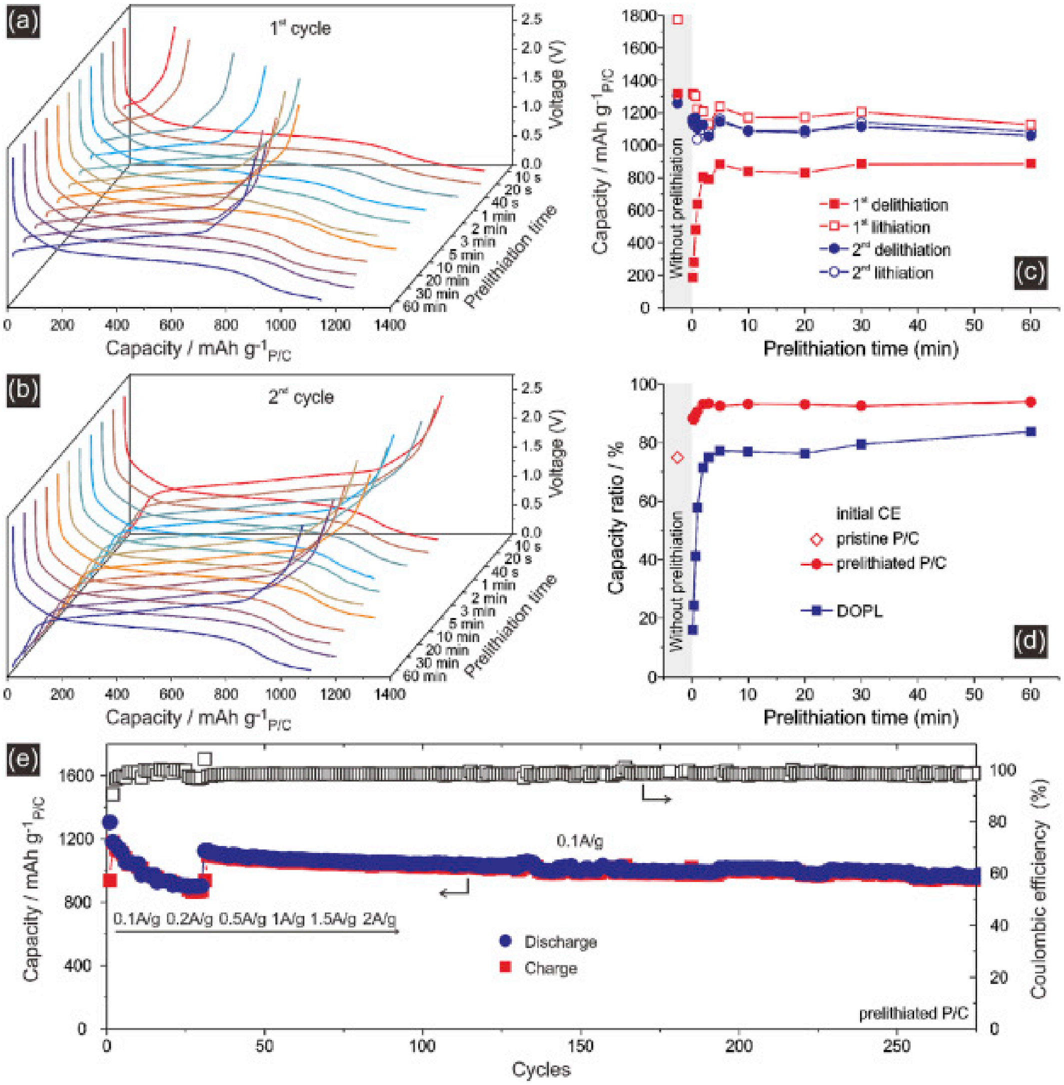

Fig. 1. The 1st (a) and 2nd (b) cycle voltage profiles of the prelithiated P/C electrodes prepared with different prelithiation durations. The corresponding capacities (c), initial CE and DOPL (d). The rate and cycling performance of a fully-prelithiated P/C electrode prepared by 10 min treatment (e).

The degree of prelithiation (DOPL), which is of vital importance to the balance of the anode/cathode capacities and thus the maximization of full-cell capacity[16], can be expressed as the ratio of 1st to 2nd delithiation capacities. As shown in Fig. 1d, the DOPL can be precisely controlled by treatment duration. A maximum DOPL of ~ 80% is reached just after 5 min of immersion, indicating a high efficiency of this prelithiation. The ~ 20% unprelithiated reversible capacity is probably from the contribution of carbon materials in the electrode. The initial CE of the prelithiated anode can be described by the ratio of 2nd delithiation/1st lithiation capacities. Obviously, the prelithiated P/C electrodes exhibit a much higher initial CE than that of the pristine P/C electrode (Fig. 1d). Even with a 10 second treatment (DOPL = 16%), the initial CE can be improved from 74% to 88%. For the fully-prelithiated P/C electrode (DOPL = 80%), the initial CE is as high as 93%. It is worth pointing out that the DOPL represents the reversible chemical Li insertion, while CE is determined by the formation of SEI layer. Apparently, during the chemical prelithiation, an artificial SEI layer is formed on the P/C anode's surface and the formation of this artificial SEI layer is much faster than Li insertion.

SEM was used to observe the surface morphologies of the pristine and prelithiated P/C electrodes (Fig. 2). After chemical prelithiation, the nanowires clearly become thicker because of volume expansion. Notably, the surface turns to be smoother, which is evidence for the artificial SEI layer formed on the prelithiated P/C. Since there is still 7% of uncompensated capacity loss even after the complete prelithiation (DOPL = 80%), the artificial SEI layer may undergo a slight reconstruction during cell cycling. Ex-situ Raman spectroscopy and XPS analysis were further applied to confirm the presence of artificial SEI layer and study its reconstruction. The initial (P-1 and Li-P-1) and final (P-2 and Li-P-2, being discharged to 0.77 V) state for the pristine and prelithiated P/C electrodes were separately characterized (Fig. 3a). As shown in Fig. 3b, the peaks at 1320 cm^{-1} and 1560 cm^{-1} are attributed to D and G band of carbon. Compared with P-1, there are a few new peaks (marked by dash lines) observed for Li-P-1, and both P-2 and Li-P-2 also have these extra peaks, suggesting a similar composition between the artificial SEI layer on Li-P-1 and the electrochemical generated SEI layer on P-2 as well as Li-P-2. For Li-P-1 and Li-P-2, the increased intensity of the peaks at 430 cm^{-1} and 800 cm^{-1} may be indicative of the reconstruction of artificial SEI layer during cell cycling. The above observation is also consistent with XPS results. As shown in Fig. 3c, P-2, Li-P-1 and Li-P-2 have an extra C 1s peak around 290 eV in comparison with P-1, corresponding to the formation of artificial SEI layer during chemical prelithiation. While the Li 1s, P 2p, C 1s and F 1s for Li-P-1 and Li-P-2 are quite different, also indicating the reconstruction of artificial SEI layer after electrochemical cycling.

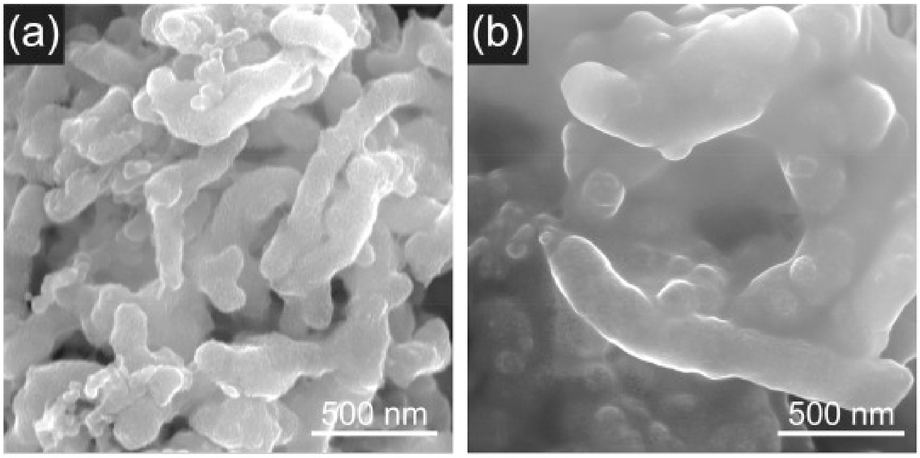

Fig. 2. SEM images of the pristine (a) and prelithiated (b) P/C electrode.

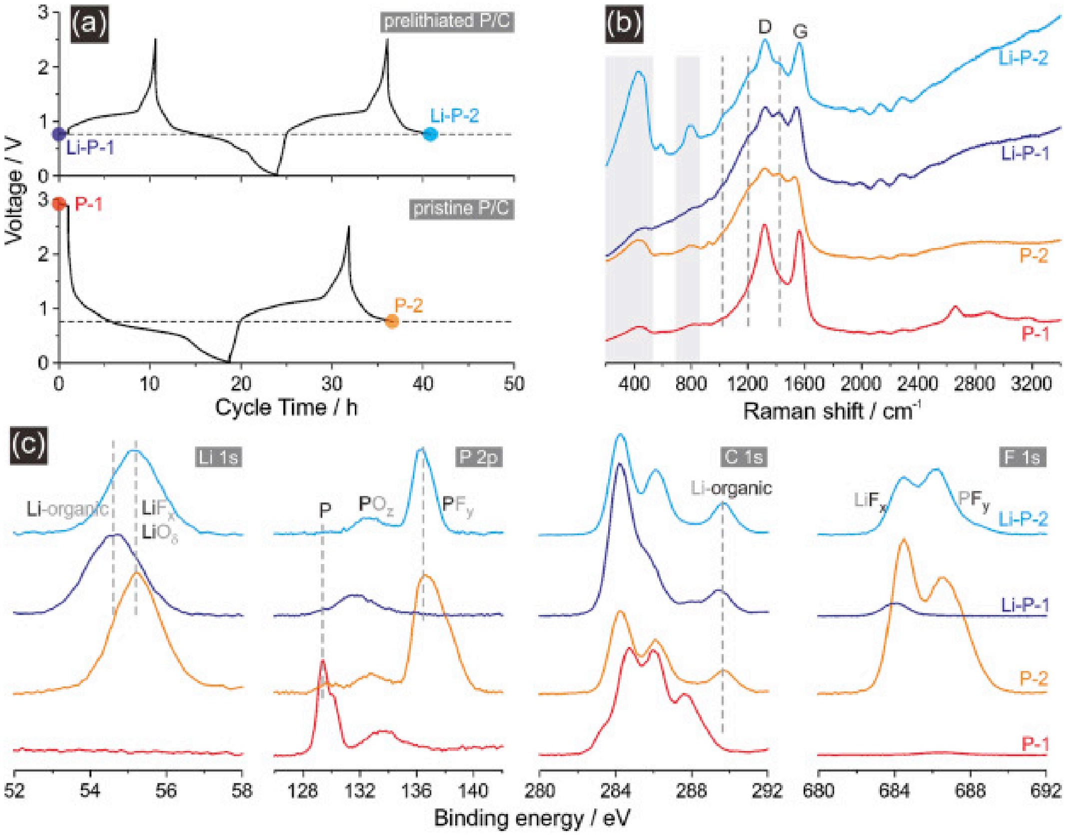

Fig. 3. Voltage profiles of the pristine and fully-prelithiated P/C electrodes (a), P-1 and Li-P-1 are the initial state, P-2 and Li-P-2 are the final state which both electrodes were electrochemical discharged to the open circuit voltage for a freshly assembled Li-P-1 half cell, namely, 0.77 V. Raman spectra (b) and Li 1s, P 2p, C 1s, F 1s XPS spectra (c) of P-1, P-2, Li-P-1 and Li-P-2. The possible species corresponding to each XPS peak are given in the figure.

Although the reconstruction of artificial SEI layer still need to consume some active Li ions, this additional consumption could be compensated by the preloaded active Li ions inside the prelithiated P/C composite as schematically illustrated in Fig. 4b. In this case, the full-cell capacity could be maximized. It should be noted that this requires a delicate control of DOPL (Fig. S4), which can be easily realized by the reported chemical prelithiation method, to carefully control the treatment duration. To assemble full LIBs and verify the prelithiation efficiency, a commercial $LiCoO_2$ (LCO) was chosen as the cathode active material. When paired with the pristine P/C electrode (Fig. 4a), the resulting LCO vs. P/C LIB exhibits an initial charge capacity of 114 mAh g^{-1}_{LCO} and discharge capacity of 36 mAh g^{-1}_{LCO} at 1 C rate (Fig. 4c). A large amount of active Li ions from LCO are consumed for SEI formation on the P/C electrode (Fig. 4a). Thus, the reversible capacity for LCO vs. P/C LIB is below 50 mAh g^{-1}_{LCO} at 1 C (Fig. 4d). In contrast, when paired with a partly-prelithiated P/C electrode prepared by 20 s treatment in 1 M Li-Bp/THF (Fig. 4b), the resulting LCO vs. partly-prelithiated P/C LIB demonstrates an initial charge capacity of 114 mAh g^{-1}_{LCO} and a stable discharge capacity of 104 mAh g^{-1}_{LCO} at 1 C rate, which are close to those of the LCO in a half cell using Li foil as the counter electrode (Fig. 4c). Moreover, the LCO vs. partly-prelithiated P/C LIB exhibits an excellent cycling stability at 1 C rate. It maintains a reversible capacity over 100 mAh g^{-1}_{LCO} over 2000 cycles. Except for a relatively low CE of 91.9% in the 1st cycle owing to the restabilization of SEI layer, the subsequent CE is nearly 100% in every cycle (Fig. 4e).

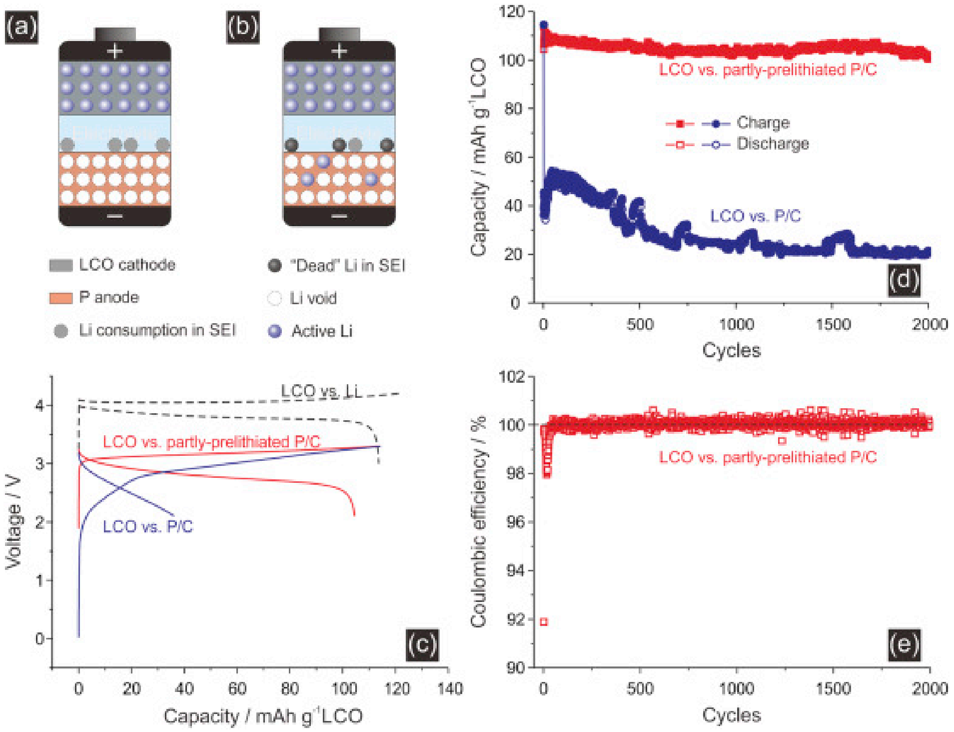

Fig. 4. Schematic illustration of the LCO vs. P/C LIB (a) and the LCO vs. partly-prelithiated P/C LIB (b). The 1st cycle voltage profiles (c) and cycling performance (d) at a rate of 1 C (1 C = 140 mAh g^{-1} of LCO). The corresponding CE of LCO vs. partly-prelithiated P/C LIB (e).

Apart from compensating the initial capacity loss due to the consumption of active Li ions during the formation of SEI layer, the anode prelithiation also enabled the pairing with Li-free cathodes. Sulfur stands as a promising Li-free cathode materials due to its high theoretical capacity (1675 mAh g^{-1})[29]. It is usually paired with a Li metal anode. Although Li-S batteries promise a high theoretical energy density, the Li metal anode remains a big obstacle because of its low CE and serious safety concern[30]. A fully-prelithiated P/C electrode can be used to replace the Li metal anode. Fig. 5a schematically illustrates a full cell made with fully-prelithiated P/C anode and S/C cathode. As shown in Fig. 5b and 5c, the resulting S/P cell exhibits a good rate capability and cycling stability in spite of a limited Li source. At 1 A/g, it delivers an initial capacity of 460 mAh $g^{-1}_{S/C}$ and retains a reversible capacity of 312 mAh $g^{-1}_{S/C}$ after 300 cycles, with a capacity decrease of 0.10% per cycle and an average CE over 99%. It demonstrates discharge capacities of 686, 589, 485, 421, 363, and 327 mAh $g^{-1}_{S/C}$ at 0.1, 0.2, 0.5, 1, 1.5, and 2 A g^{-1}, respectively. When the current density is back to 0.1 A g^{-1}, it delivers a reversible capacity of 681 mAh $g^{-1}_{S/C}$. As shown in Fig. 5d, the S/P cell exhibits similar voltage profiles as the S/C half cell except at different voltages (Fig. S5), displaying two discharge plateaus at 1.4 V and 1.1 V at 0.1 A g^{-1}. Despite the output voltage being a little low, the newly configured S/P cell could provide a theoretical maximum energy density of 967 Wh kg^{-1}, which is higher than most LIBs consisting of sulfur cathode and other lithiated anodes (Fig. S8), since both S and P have high specific capacities. An energy density of 358 Wh kg^{-1} has been realized based on the total mass of active materials (P/C and S/C) and the discharge capacity at 0.1 A g^{-1} (Fig. 5d inset, see details in Supporting Information). In addition, both S and P are cheap and environmentally abundant. These characteristics make the newly configured S/P cell a potential candidate for next-generation batteries.

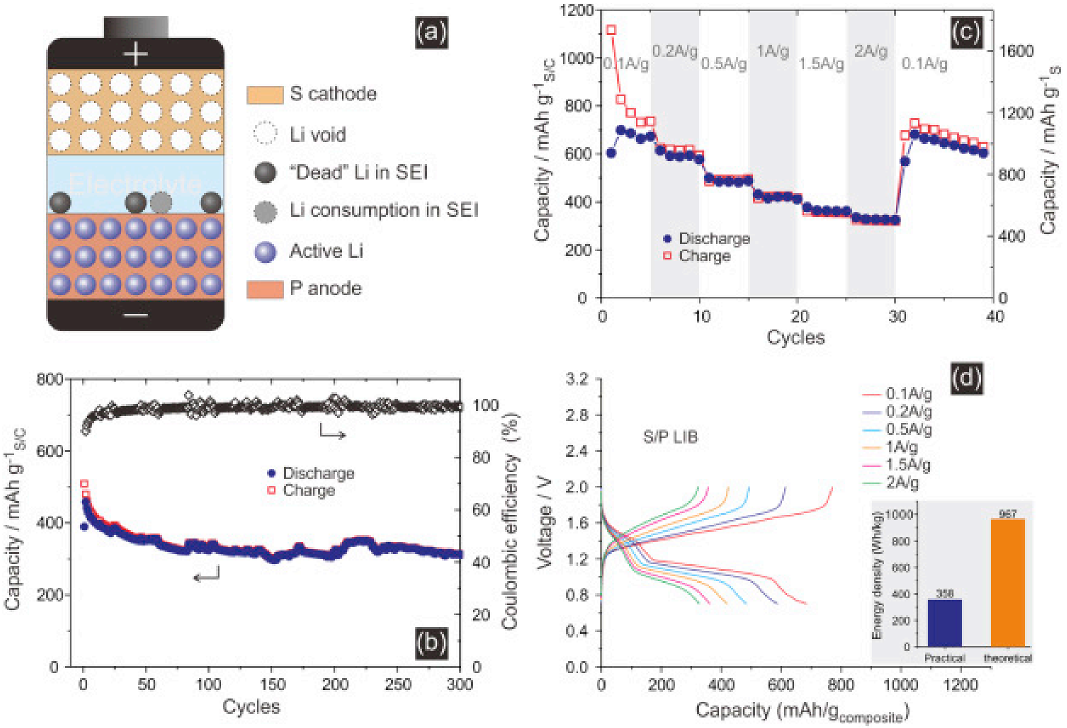

Fig. 5. Schematic illustration of the S/P LIB (a). Cycling performance of the S/P LIB at 1 A $g^{-1}_{S/C}$ (b). Rate performance of the S/P LIB (c). Typical voltage profiles at different current densities (d). Insert is the theoretical and practical energy densities of the S/P LIB.

4. Conclusions

In summary, we demonstrated a controllable chemical prelithiation of P/C composite electrodes, and that the DOPL can be easily controlled by adjusting the treatment duration. The prelithiated P/C electrodes with certain DOPL were tested in full cells with a Li containing LCO and a Li-free sulfur cathode. In comparison with the LCO vs. P/C, the LCO vs. partly-prelithiated P/C delivered a higher reversible capacity of ca. 104 mAh g^{-1}_{LCO} at 1 C, suggesting an effective compensation for the initial active Li ions loss by prelithiation. The newly configured S/P cell demonstrated a good cycling performance and rate capability. The theoretical maximum energy density for S/P LIB is as high as 967 Wh kg^{-1}, and an energy density of 358 Wh kg^{-1} has been achieved in the present study. We expect that this chemical prelithiation could be extended to the development of high-capacity LIBs using other electrode materials.

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