



# Lithium tin phosphate anode partially reduced through prelithiation for hybrid capacitor application



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## ABSTRACT

Incorporated as the negative electrode, the  $\text{LiSn}_2(\text{PO}_4)_3$  (LSP) crystals requires a prelithiation step to decompose LSP partially and yield tin metal for a relatively steadied capacity in cycling the hybrid capacitor of  $\text{LiPF}_6$  electrolyte. The charge transfer reactions of lithium alloying tin at low potentials offer a substantial amount of electrical capacity. Hence, several capacitors of LSP negative and activated carbon (AC) positive are prepared to understand the effects of prelithiation and LSP:AC mass ratio on how to exploit this electrochemical capacity. Among two prelithiation levels and three mass ratios, the combination of LSP-I (10% tin) and 1:1 (LSP:AC) mass ratio stands out as the best choice over a wide range of specific current. On the other hand, the selection of a specific current low enough to match the charge-transfer reaction kinetics enables the LSP electrode of high prelithiation level, LSP-II (45% tin), to utilize its battery-like capacity thoroughly. The maximum energy of hybrid capacitor LSP-II/AC is measured  $28.7 \text{ W h kg}^{-1}$  at a minimum specific current  $0.03 \text{ A g}^{-1}$ .

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## 1. Introduction

Instead of employing two electrodes of high-surface-area carbons, the lithium ion hybrid capacitors (LIHC) substitute one of the two electrodes relying on double-layer capacitance with a battery-like electrode. The double-layer electrode is generally swift in response, durable in cycling, but small in specific capacity. On the other hand, the battery-like electrode stores more energy, but its response is usually limited by the involved electrochemical reaction rates. Various forms of hybridization have been devised to mix the two mechanisms of double layer capacitance and faradaic charge-transfer reactions. Preceding research efforts point out that the properties of LIHC are more than a simple combination of two dissimilar electrodes in series. For those kinetics-related properties, an individual rate-determining step often controls the hybrid behavior and manifests itself in the capacitor operation under specific conditions [1–4].

Technically, the internal serial design of LIHC allows either the positive or the negative electrode to implement active materials of reversible insertion/deinsertion or charge-transfer reaction, meanwhile the other electrode undergoes ion adsorption/desorption.

The hybrid capacitors of negative battery electrode generally outperform other types of LIHC, thanks to the in-depth knowledge on anode materials of lithium ion battery. Negative electrodes of lithiated graphite [5–7], hard carbons [8,9], soft carbons [10,11] have been chosen to match with the activated carbon (AC) positive electrode. These combinations permit the applied voltage window slightly over 4.0 V, since their negative electrode potentials maintain quite flat, 0.5–0.1 V (vs.  $\text{Li/Li}^+$ ), during charge/discharge. The wide voltage window enables the cell energy density four or five times the value of electrochemical capacitor of double layer capacitance. In contrast, the applied voltage window is limited to 2.5–3.5 V for the hybrid capacitors of a positive battery electrode, for example, the positive  $\text{LiFePO}_4$  [12],  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_4$  [13]. Their energy densities, therefore, are moderately higher than the conventional double layer capacitor. An excellent overview of LIHCs and a discussion on their strengths and weaknesses have been given by Aravindan and coauthors [14].

Members of the nasicon family are known for their fast ion conductivities, considered as popular electrode candidates for hybrid capacitor [15–19].  $\text{LiSn}_2(\text{PO}_4)_3$  (abbreviated as LSP) crystallizes in a monoclinically distorted nasicon-type structure [20]. When being lithiated at low potentials, the LSP powder decomposes to yield tin metal. The metallic tin phase is subsequently alloyed with lithium in charge/discharge operation. Electrochemical alloying reactions of tin metal involve a substantial amount of electrical energy,

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accompanied with huge volume changes [21–24]. Therefore, decomposed LSP could be viewed as a host matrix for tin, cushioning the cycling strains caused by electrochemical reactions of tin alloying. The capacity of LSP has been reported to be  $320 \text{ mA h g}^{-1}$  after 50 cycles, which is comparable to the theoretical capacity of graphite anode [25].

In this work, we fabricate two half cells of Li/LSP and Li/AC, along with the hybrid cells of LSP/AC to study their capacities and degradation during cycling. On the hybrid capacitor, two major fabrication factors are chosen to investigate; the prelithiation level and the LSP:AC mass ratio. Prelithiation refers to the reduction treatment that we carry out before assembling a hybrid LSP/AC capacitor. The reduction treatment partially decomposes the LSP crystal to certain level and stabilizes the cycling performance of the hybrid capacitor. Our results indicate the LSP capacity relies on the electrochemical reactions of lithium alloying tin, which demand the low current conditions to manifest them.

## 2. Materials and methods

Lithium tin phosphate (LSP) powder was synthesized through conventional solid state reaction using reagent-grade chemicals. The synthesis started with weighing a calculated amount of  $\text{Li}_2\text{CO}_3$  (Aldrich, 30% in excess),  $\text{SnO}_2$  (99.9%, ACROS), and  $\text{NH}_4\text{H}_2\text{PO}_4$  (99.8%, ACROS) and mixing through ball milling for 2 h. The precursor mixture was calcined at  $800^\circ\text{C}$  in furnace for 10 h, and pulverized with pestle and mortar. Excess lithium was necessary. If the LSP powder was synthesized without excess lithium, the strongest and the next strongest lines of tin oxide emerged in the X-ray diffraction pattern. To prepare the negative electrode, the calcined LSP powder 0.95 g was first ball-milled with 0.05 g Super P® (TIMCAL Graphite and Carbon) for 12 h. The resulting mixture was labeled as c-LSP. A slurry was then prepared through blending 80 wt% c-LSP, 10% Vulcan® XC72R (Cabot), 10 wt% PVdF binder (Aldrich), and a suitable amount of 1-methyl-2-pyrrolidinone (NMP) liquid vehicle. The LSP electrode was prepared by dispersing the slurry on a copper disk of 2 cm in diameter, and drying in a vacuum oven at  $80^\circ\text{C}$ , following by 1.5 ton uniaxial pressing. The active material mass was estimated as the weight difference between the dry electrode and the copper disk. In making the Li/LSP half cell, an LSP electrode was housed in an electrochemical test cell (SC-Basic, MikroMasch), with a  $25 \mu\text{m}$  microporous separator (Celgard 2500) stacked on top. In the following step, we dipped the electrolyte of 1.0 M  $\text{LiPF}_6$  in ethylene carbonate (EC) and dimethyl carbonate (DMC) solution. Then, a piece of lithium metal foil (99.9%, Alfa Aesar) was placed on top of the separator and the test cell was closed firmly.

With the setup of Li/LSP cell, we conducted the prelithiation treatment of LSP electrode, in which two types of electrode were prepared, namely, LSP-I and -II. For a low level of lithiation, the LSP-I electrode underwent three charge/discharge cycles between 2.0 and 0.01 V (vs.  $\text{Li/Li}^+$ ) at  $100 \text{ mA g}^{-1}$ . For a high level of lithiation, the LSP-II electrode experienced five charge/discharge cycles between 2.0 and 0.01 V (vs.  $\text{Li/Li}^+$ ) at  $300 \text{ mA g}^{-1}$ . After prelithiation, the lithium foil was removed and substituted with the AC electrode, and more electrolyte was added. In this manner, the LSP/AC cell was assembled. In the LSP/AC cell, the sandwich of copper disk, LSP electrode, separator, AC electrode, and aluminum disk was pressed tightly under a spring of 20 newton force. Three mass ratios of LSP:AC had been implemented, including 1:0.5, 1:1, and 1:2.

The AC positive electrode was prepared through dispersing the AC slurry on top of a current collecting aluminum disk of 2.0 cm in diameter. The AC slurry contained 80 wt% of activated carbon (BET surface area  $\sim 2400 \text{ m}^2 \text{ g}^{-1}$ , grade 4/70, 3J&J Pharma Ltd.), 10 wt% of Vulcan carbon, and 10 wt% of PVdF binder in the NMP solvent. The Li/AC cell was assembled in the same way as the Li/LSP cell. All the above processing steps were performed in an argon-filled glove box (GB-100, SunRay Science), so were those electrochemical measurements. The glove box was equipped with a load lock vacuum chamber and a gas circulating/purifying system to keep oxygen and water impurity  $<1 \text{ ppm}$ .

Galvanostatic charge/discharge experiments and cycle stability tests were controlled and recorded with a potentiostat (5000 Workstation, Jiehan). Variations of the electrode potentials during charge/discharge were measured using a multi-channel workstation (1470E, Solartron). The capacitance of AC electrode was measured on a Li/AC cell with cyclic voltammetry (CV), using a three-electrode setup of the MikroMasch cell along with the lithium metal reference.

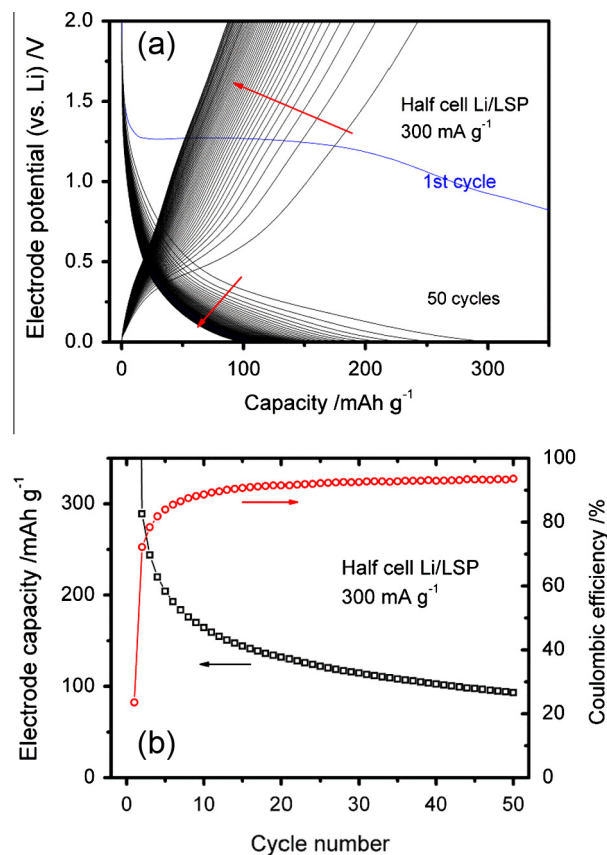
The crystal structure of LSP powder was analyzed before and after prelithiation using an X-ray diffractometer (D2 Phaser, Bruker), which was equipped with a copper  $\text{K}\alpha$  radiation source (wavelength 0.15406 nm) and nickel filter. The LSP electrode surface was examined using a scanning electron microscope (SEM, JSM-6390 JEOL). Nitrogen adsorption-desorption isotherms of the grade 4/70 AC were measured with a surface area and pore size analyzer (AUTOSORB-1, Quantachrome).

## 3. Results and discussion

### 3.1. LSP and AC electrodes

Fig. 1(a) presents the charge/discharge characteristics of as-prepared LSP at  $300 \text{ mA g}^{-1}$  in the potential range 2.0 and 0.01 V (vs.  $\text{Li/Li}^+$ ). The first discharge cycle shows an irreversible plateau of  $\sim 200 \text{ mA h g}^{-1}$  capacity at 1.3 V (vs.  $\text{Li/Li}^+$ ), which vanishes in the subsequent charge and discharge cycles. The capacity of the first discharge cycle is huge,  $\sim 1030 \text{ mA h g}^{-1}$ . The capacity of the second discharge plunges to  $289 \text{ mA h g}^{-1}$ , approximating that of the first charge cycle,  $243 \text{ mA h g}^{-1}$ . More details on the decreasing electrode capacity are plotted in Fig. 1(b), showing a quick slow-down during the first three discharge cycles. At the end of 50 cycles, the discharge capacity drops to  $93 \text{ mA h g}^{-1}$ . On the other hand, the coulombic efficiency increases with increasing cycle number. The coulombic efficiency exceeds 90% after the early 12 cycles. In view of abnormal capacity of the first discharge cycle and the irreversible plateau, we presume the LSP crystal, instead of being a stable lithium host, have been reduced below 1.3 V vs. Li.

Phase analysis confirms the decomposition of LSP during electrochemical lithiation. Fig. 2(a) shows a typical diffraction pattern of the as-prepared LSP powder. The diffraction positions at  $2\theta = 14.5^\circ, 20.0^\circ, 21.0^\circ, 24.2^\circ, 29.3^\circ, 32.1^\circ, 36.3^\circ, 36.9^\circ$ , and their relative intensities agree well with those known for monoclinic  $\text{LiSn}_2(\text{PO}_4)_3$  crystal (JCPDS 49-1175). On the other hand, Fig. 2(b) and (c) show these explicit but fading LSP diffractions on top of a



**Fig. 1.** Galvanostatic charge/discharge of the Li/LSP cell. (a) LSP electrode potential is plotted against capacity for 50 cycles. The electrode, containing 0.88 mg  $\text{LiSn}_2(\text{PO}_4)_3$ , is charged and discharged at  $300 \text{ mA g}^{-1}$  between 2.0 and 0.01 V (vs.  $\text{Li/Li}^+$ ). The trace of the first discharge cycle is out of the graph range,  $\sim 1030 \text{ mA h g}^{-1}$ . (b) Variations in discharge capacity and coulombic efficiency are plotted vs. the cycle number.

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