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## All-solid-state planar integrated lithium ion micro-batteries with extraordinary flexibility and high-temperature performance

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## ARTICLE INFO

## Keywords:

Graphene

Planar

Lithium ion micro-batteries

High temperature

Flexible

## ABSTRACT

The relentless development and modularization of electronics have urgently required the all-round improvement of performance, flexibility, safety, miniaturization and integration of micro-batteries. However, traditional cell design in stacked geometry fails to meet these comprehensive demands, especially high-temperature performance. Herein, we report the prototype construction of all-solid-state planar lithium ion micro-batteries (LIMBs), with characteristics of superior volumetric energy density, exceptional flexibility, extraordinary high-temperature performance, and outstanding integration of bipolar cells. The planar LIMBs were manufactured based on the interdigital patterns of lithium titanate nanospheres/graphene as anode and lithium iron phosphate microspheres/graphene as cathode, free of polymer binder and separator, working in ionogel electrolyte. The resulting LIMBs deliver ultrahigh volumetric energy density of  $125.5 \text{ mWh cm}^{-3}$ , ultralong-term cyclability without capacity loss after 3300 times at room temperature, and outstanding rate capability due to the multi-directional Li-ion diffusion mechanism. Furthermore, our micro-batteries present exceptional flexibility without capacity decay under repeated bending, remarkable high-temperature performance up to 1000 cycles operated at  $100^\circ\text{C}$ , superior miniaturization and simplified modularization of constructing integrated LIMBs that readily control over the output voltage and capacity, all of which can't be simultaneously achieved by the conventional techniques. Therefore, our planar LIMBs hold tremendous opportunities for future miniaturized and integrated electronics.

## 1. Introduction

The rapid boom on smart wearable and integrated electronics, largely driven by Moore's Law, has urgently stimulated the never-ceasing demand of advanced intelligent energy storage systems with high performance, miniaturization, mechanical flexibility, light weight and high-temperature performance stability [1–8]. Lithium ion batteries (LIBs) are the primary popular batteries [9–12], but appear to have critical shortcomings of fixed shapes, large size, bulk volume, heavy weight, originating from the stacked device geometry [13–16]. Furthermore, such stacked LIBs also suffer from several inherent limitations of liquid electrolyte leakage, flammability and volatility of electrolyte, unsatisfactory safety and flexibility, lacking versatility and integration in form factors for multi-functional on-chip power source-utilized electronics [17–22].

To overcome these obstacles, great efforts have been devoted to developing planar microscale energy storage systems, e.g., micro-

batteries (MBs) [23–25] and micro-supercapacitors [26–28], as a promising class of the distributive power sources. Typically, they integrate all the device components, such as two opposite electrodes, electrolyte, and current collectors, on a single planar substrate, which show substantial superiority over the stacked geometry, and fully enable robustness in terms of flexibility, miniaturization and integration of electronics. So far, enormous attentions have been focused on the rational fabrication of ion-electron conductive and compact electrodes, manufacture of high-resolution electrode micro-patterns, utilization of metal or metal-free current collectors [29,30], aiming to enhance energy density of different-type planar MBs, including lithium ion micro-batteries (LIMBs) [29,31,32], Zn//MnO<sub>2</sub> MBs [33,34], Zn//Ag<sub>2</sub>O batteries [35], Zn//LiMn<sub>2</sub>O<sub>4</sub> (LMO) [36] and Zn//LiFePO<sub>4</sub> (LFP) batteries [36]. Among them, planar LIMBs are currently regarded as a highly competitive candidate for on-chip energy storage due to large voltage window, lightweight and high energy density. For instance, LIMBs

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<https://doi.org/10.1016/j.nanoen.2018.07.009>

Received 15 May 2018; Received in revised form 13 June 2018; Accepted 5 July 2018

Available online 07 July 2018

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based on  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO)//LMO or LTO// $\text{LiCoO}_2$  displayed excellent rate capability and robust integration, however the photolithography technique employed is complex and consists of multiple steps [32,37,38]. 3D planar LIMBs with three-dimensional NiSn and lithiated  $\text{MnO}_2$  could exhibit high power density, but represented inferior cycling stability [29,30]. Further, 3D printed LTO//LFP-LIMBs could present highly enhanced areal capacity, but suffer from limited rate capability due to low electrical conductivity of 3D electrodes [31,39]. Despite some significant advances in this field, developing planar integrated LIMBs with satisfied flexibility, high-temperature performance and modularization has not yet been achieved.

Here, we for the first time demonstrate the on-chip construction of all-solid-state planar integrated LIMBs (denoted as LTO//LFP-LIMBs), with extraordinary energy density, robust flexibility, high-temperature performance, and outstanding integration, based on the mask-assisted interdigital patterns of lithium titanate (LTO) nanospheres anode and lithium iron phosphate (LFP) microspheres cathode, in which high-quality electrochemically exfoliated graphene (EG) nanosheets were chosen as metal-free current collectors and conducting additives for establishing well-developed electrical conductive microelectrodes. The resulting LTO//LFP-LIMBs, using ionogel electrolyte, presented ultrahigh volumetric energy density of 125–146  $\text{mWh cm}^{-3}$  due to the merits of multi-directional  $\text{Li}^+$  transport. Moreover, our all-solid-state LTO//LFP-LIMBs free of separator exhibited stable electrochemical performance without apparent capacity degradation after long-term 3300 cycles at room temperature, and exceptionally stable flexibility under various bending shapes, and remarkable modular integration of bipolar cells for boosting output voltage and capacity without requirement of metal interconnection. Notably, our LIMBs could be stably operated at high temperature of 100 °C with greatly improved performance and long-term cyclability due to the use of high-stable ionogel electrolyte.

## 2. Experiment

### 2.1. Materials preparation

LTO nanospheres were prepared from the TiN precursor via hydrothermal treatment [40]. Briefly, TiN (0.25 g) nanopowders, hydrogen peroxides (16 mL, 30 wt%) and ammonia solution (6 mL, 25–28 wt%) were added into 28 mL deionized water and continuously stirred for 30 min. Subsequently, deionized water (50 mL) and ethanol (100 mL) were mixed with the above dispersion for further hydrolysis of peroxo-titanium complex from the oxidation of TiN. Then,  $\text{LiOH}\cdot\text{H}_2\text{O}$  (0.14 g) and polyvinyl pyrrolidone (100 mg) were added into the resulting dispersion under the constant stirring until white amorphous  $\text{TiO}_2/\text{Li}^+$  nanospheres were obtained. After the white powder was annealed at 750 °C for 7 h in Ar gas, the product of LTO coated with carbon layers was achieved. LFP microspheres, purchased from Dong Guan General Exploring Battery Technology Co., Ltd, were further treated at the ethanol dispersion through ultrasonication for 1 h. Then, the resultant dispersion was kept undisturbed for 10 min, and the small LFP microspheres dispersed at the top were collected through filtration for further usage. EG was prepared by electrochemical exfoliation of graphite at aqueous KOH solution, as reported previously [41].

### 2.2. Ionogel electrolyte

Ionogel electrolyte was prepared according to our reported work [42]. First, bis(trifluoromethanesulfonyl)imide lithium salt ( $\text{LiTFSI}$ ) was added into 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ( $\text{P}_{14}\text{TFSI}$ ) under stirring to form 1 M  $\text{LiTFSI-P}_{14}\text{TFSI}$  and 0.2 g poly(vinylidene difluoride-co-hexafluoropropylene) (PVDF-HFP) was mixed with acetone ( $\sim 2$  mL) under continuous stirring to form uniform transparent solution. Afterward, 2.5 g  $\text{LiTFSI-P}_{14}\text{TFSI}$  was dropwise added into PVDF-HFP solution, and then the ionogel electrolyte of  $\text{LiTFSI-P}_{14}\text{TFSI-PVDF-HFP}$  was obtained.

### 2.3. Fabrication of LTO//LFP-LIMBs

First, 3 mL EG ethanol dispersion ( $0.1 \text{ mg mL}^{-1}$ ) was filtrated through the interdigital home-made mask with eight fingers (length of 14 mm, width of 1 mm, interspace of 0.5 mm) to form the high electrical conductive EG layer on a nylon membrane ( $0.22 \mu\text{m}$ , Agela Technologies). Second, 1 mL LTO/EG dispersion ( $0.5 \text{ mg mL}^{-1}$ , 10 wt% EG) and 1 mL LFP/EG dispersion ( $0.5 \text{ mg mL}^{-1}$ , 10 wt% EG) were followed from each side (four fingers) of the mask under constant filtration to establish anode and cathode, respectively. After removing the mask, LTO//LFP-LIMBs were achieved. For comparison, LTO//LFP-LIMBs with EG cover (denoted as LTO//LFP-LIMBs-C) was also constructed through the additional filtration of the top EG layer (3 mL,  $0.02 \text{ mg mL}^{-1}$ ) on LTO and LFP microelectrodes, and other steps were kept the same as LTO//LFP-LIMBs. Subsequently, ionogel electrolyte dispersion was carefully drop-costed on the surface of electrode films and solidified at 80 °C for 12 h in a vacuum condition. Finally, the conductive Cu adhesive tapes (SPI SUPPLIES) were used to connect microelectrode fingers to external circuit for electrochemical measurements.

### 2.4. Materials characterizations

The morphology and structure of LTO nanospheres, LFP micro-particles, EG, and the microelectrodes of LTO and LFP were carried out using scanning electron microscopy (SEM, JSM-7800F), high-resolution transmission electron microscopy (HRTEM, JEM-2100), X-ray diffraction (XRD, X'pert Pro), and four-point probe equipment (RTS-9). Thermogravimetric analysis (TGA, STA 449 F3) was applied to evaluate the thermal stability of ionogel electrolyte. The ionic conductivity ( $\sigma$ ) of ionogel electrolyte as a function of temperature was tested by electrochemical impedance spectroscopy (EIS) at the frequency from 100 kHz to 0.1 Hz with an AC amplitude of 5 mV, based on a cell of stainless steel/ionogel electrolyte/stainless steel. The value of  $\sigma$  was calculated by the equation:  $\sigma = L/(R \cdot S)$ , where  $L$  is the length of ionogel electrolyte film,  $R$  is equivalent series resistance (ESR) from EIS,  $S$  is the geometric area of ionogel electrolyte film.

### 2.5. Electrochemical measurement

Galvanostatic charge and discharge (GCD) profiles were performed by LAND CT2001A battery tester with the voltage between 1.0 and 2.4 V at current densities from 0.2 to 60 C. Cyclic voltammetry (CV) curves at 0.1 or 0.2  $\text{mV s}^{-1}$  and EIS spectra from 100 kHz to 0.01 Hz with an AC amplitude of 5 mV were measured on electrochemical workstation (CHI760E). The electrochemical performance of LIMBs at 100 °C was kept at the tested temperature in a thermostat box with constant temperature mode for 1 h until equilibration. For the half cell, the working electrode, composed of active material (LTO or LFP), carbon black and polyvinylidene fluoride with the weight ratio of 80:10:10, was tested in 1 M  $\text{LiTFSI-P}_{14}\text{TFSI}$  using lithium plate as reference and counter electrode.

## 3. Results and discussion

The fabrication and modular integration of all-solid-state LTO//LFP-LIMBs based on interdigital LTO anode and LFP cathode was schematically illustrated in Fig. 1, in which high-conductive EG nanosheets ( $\sim 1000 \text{ S cm}^{-1}$ , Figs. S1 and S2) were used as current collectors, 2D conducting additives and flexible elastic support. First, the ultrathin bottom layer of EG interdigital patterns (8 fingers) was directly deposited by mask-assisted filtration of EG ink (Fig. 1). Second, the asymmetric interdigital LTO and LFP layers were built by controlled deposition of anodic LTO/EG and cathodic LFP/EG on the four fingers at each side of the mask, respectively, on a nylon membrane with a uniform smooth surface (Fig. S3). High-crystalline LTO nanospheres,

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