# Multi-Layer Printable Lithium Ion Micro-Batteries with Remarkable Areal Energy Density and Flexibility for Wearable Smart Electronics

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Pursuing high areal energy density and developing scalable fabrication strategies of micro-batteries are the key for the progressive printed microelectronics. Herein, the scalable fabrication of multi-layer printable lithium ion micro-batteries (LIMBs) with ultrahigh areal energy density and exceptional flexibility is reported, based on highly conductive and mechanically stable inks by fully incorporating the polyurethane binders in dibasic esters with high-conducting additives of graphene and carbon nanotubes into active materials to construct a cross-linked conductive network. Benefiting from relatively higher electrical conductivity ( $\approx$ 7000 mS cm<sup>-1</sup>) and stably connected network of microelectrodes, the as-fabricated LIMBs by multilayer printing display robust areal capacity of 398  $\mu$ Ah cm<sup>-2</sup>, and remarkable areal energy density of 695  $\mu$ Wh cm<sup>-2</sup>, which are much higher than most LIMBs reported. Further, the printed LIMBs show notable capacity retention of 88% after 3000 cycles, and outstanding flexibility without any structure degradation under various torsion states and folding angles. Importantly, a wearable smart bracelet, composed of a serially connected LIMBs pack, a temperature sensor, and a light-emitting diode, is realized for the automatic detection of body temperature. Therefore, this strategy of fabricating highly conductive and mechanically stable printable ink will open a new avenue for developing high-performance printable LIMBs for smart microelectronics.

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#### DOI: 10.1002/smll.202104506

### 1. Introduction

With recent advances in radio frequency identification tag,<sup>[1]</sup> active matrix addressed displays,<sup>[2]</sup> self-powered systems,<sup>[3-5]</sup> wearable electric sensing systems<sup>[4,6-9]</sup> and emerging internet of things, it is not hard to imagine a future with interconnected electronic devices, realizing overall recognition of objects, intelligent processing and reliable transmission of captured information. To conform with such dramatic development, it is of critical importance to explore lowcost, flexible and high-energy-density microscale electrochemical energy storage devices for powering the aforementioned systems. So far, rapid innovations in advanced manufacturing technologies for microdevices, such as 3D printing,[10-17] inkjet printing,<sup>[18,19]</sup> stencil printing,<sup>[20]</sup> mask-assisted filtration,<sup>[21-23]</sup> and spraycoating,<sup>[24,25]</sup> have enabled devisable construction and diversified modality. Considering the flexibility of process, costeffectiveness and large-batch production, screen printing technique has become a

promising candidate for scalable fabrication of planar microdevices. Moreover, screen printing provides a universal approach for incorporating various substrates ranging from paper, wood, metals, fabric, glasses, ceramics and even to human skin<sup>[26]</sup> into the design of electronics, making them flexible, lightweight and wearable.

So far, lithium ion micro-batteries (LIMBs) fabricated by screen printing technique still suffer from limited areal energy density, mainly due to the low areal loading of active electrode materials, hampering their implementation in new energyintensive applications. Although multi-layer screen printing process can increase the areal mass loading of active materials, the electrical conductivity and lithium-ion mobility of the printed LIMBs are unsatisfying. To this end, highly conductive materials like graphene and carbon nanotubes (CNT) are introduced into the printable inks to construct a cross-bridged structure with three-dimensional (3D) conductive networks by connecting isolated electrode particles during multi-layer printing and maintain the long-range order migration of Li<sup>+</sup> and high electrical conductivity.



Achieving a highly conductive ink to enable good adhesion on various substrates is largely determined by the used types of the solvents and binders. So far, different organic binders and solvents have been extensively studied due to their compelling adhesion and compatibility.<sup>[27-29]</sup> However, given the toxicity of most organic solvents, such as toluene,<sup>[30]</sup> tetrahydrofuran,<sup>[31,32]</sup> dimethylsulfoxide,<sup>[33]</sup> N-methyl pyrrolidone,<sup>[1,34,35]</sup> and dimethyl formamide,<sup>[36]</sup> it is of great importance to develop safe, abundant and cheap solvents for ink processing. Apart from exploring the green solvents, it is very challenging to develop a binder with highly viscosity and superior mechanical stability for the fabrication of screen printing inks. In this regard, polyurethane, with characteristics of chemical resistance, resilience, mechanical properties, and low compression deformation, has been demonstrated in various field, such as automobiles, construction, and biomedicine.<sup>[37-39]</sup> Nevertheless, it is still rarely developed for preparing mechanically stable screen printing inks for high-areal-loading printable LIMBs.

Herein, we report the fast and scalable fabrication of high areal energy density LIMBs by highly conductive and mechanically stable screen printing inks, selecting polyurethane as a binder dispersing in dibasic ester and graphene and CNT as high-conducting additives, to realize robust electrochemical performance and flexibility that are readily integrable with wearable smart electronics. The viscosity-tunable screen printing inks with high electron-ion conductivity were prepared by compositing lithium iron phosphate (LFP) or lithium titanate (LTO) with conductive additives of graphene and CNT (denoted as LFP@GC, LTO@GC). Both of LTO@GC and LFP@GC inks showed the remarkable rheological behavior, resulting in highly electrical conductivity of ≈7490 mS cm<sup>-1</sup> of LTO@GC anode and ≈7280 mS cm<sup>-1</sup> of LFP@GC cathode. Therefore, the LIMBs offered high areal capacity of 398 µAh cm<sup>-2</sup>, corresponding to robust areal energy density of 695 µWh cm<sup>-2</sup> and excellent flexibility under different tortuous and folding states. Furthermore, the flexible LIMBs as the dominant power sources undertook the integration with a temperature sensor and a light-emitting diode (LED) to construct a flexible wearable smart bracelet, resulting in highly sensitive detection of body temperature.

## 2. Results and Discussion

The customized screen printing inks, e.g., LTO@GC and LFP@ GC inks, were prepared using a ball-milling method (Figure 1a), which uniformly mixed active materials (LFP or LTO), conductive carbon, graphene and CNT in polyurethane and dibasic ester. The LFP and LTO showed good crystal structure (Figure S1, Supporting Information) and the size of primary particles was between 100 and 800 nm (Figure S2, Supporting Information) and the secondary particles were distributed within  ${\approx}10~\mu m$  (Figure S3, Supporting Information). The conductive carbon and CNT present uniform dispersion (Figure S2, Supporting Information). It is noted that the hybrid conductive fillers of graphene and CNT could form an efficient conductive network to accelerate the electron transfer. For comparison, we also prepared the screen printing inks with addition of only graphene (without CNT), which was marked as LTO@G and LFP@G inks, respectively. The viscosity measurement was used

to evaluate the feasibility for screen printing. From Figure 1d,e, the storage modulus (G') and loss modulus (G") were applied to explore the rheological behavior. All of the inks showed high G' and G" with a solid-like behavior before the shear stress arrived at the yield points, e.g., LTO@GC (1526 Pa), LFP@GC (1500 Pa), LTO@G (580 Pa), and LFP@G (1485 Pa). When the shear stress over the point, the G' and G'' of the as-prepared inks decreased sharply, implying their liquid-like phenomena at the high region. The high yield points of LTO@GC, LFP@GC, LTO@G and LFP@G inks were beneficial for the immediate solidification after being rapidly extruded out. Additionally, the inks of LTO@GC, LFP@GC, LTO@G, and LFP@G exhibited high viscosities (>10<sup>4</sup> Pa s) at an initial shear rate of 0.1 s<sup>-1</sup>. With increasing the shear rate, all of them displayed decreased viscosities, suggesting a shear thinning behavior. All the merits are favorable to the transfer of the target inks onto the substrate without blocking in the mesh, and to enable the printing with well-defined micropatterns. As expected, LFP@GC, LTO@ GC, LFP@G, and LTO@G inks could be smoothly printed, in which the active materials and additives showed high uniformity at microscopic scale. Subsequently, the customized printed letters constituting "DICP" were screen-printed using LFP@GC, LTO@GC, LFP@G, and LTO@G inks, respectively (Figure 1b,c). It is emphasized that no fragmentation was observed in the printed letters, indicative of exceptional homogeneity of the inks. By using scanning electron microscopy (SEM), the conductive structures of screen-printed electrodes based on LFP@GC and LTO@GC inks and LFP@G and LTO@G inks were detected (below of "DICP" in Figure 1c). Apparently, both graphene and CNT served as a stably connected bridge between isolated electrode particles, availing highly electrical conductivity and long-range ordered migration of lithium ions. It is revealed that 3D conductive network of graphene/CNT possesses relatively higher electrical conductivity than the 2D graphene counterparts (Figure S4, Supporting Information), resulting in superior conductivity of LFP@GC (≈7280 mS cm<sup>-1</sup>) and LTO@GC (≈7490 mS cm<sup>-1</sup>) inks. In addition, the contact angle measurements of ionogel electrolyte bis(trifluoromethanesulfonyl) imide lithium salt/1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide/ poly(vinylidene difluoride-co-hexafluoropropylene (LiTFSI-P14TFSI-PVDF-HFP) and water against LFP@GC, LTO@GC, LFP@G, and LTO@G inks were conducted (Figures S5 and S6, Supporting information). It is suggested that the ionogel electrolyte exhibited superior surface wettability to the water with the as-prepared inks. What's more, it is noted that the screenprinted LIMBs showed mechanically stable structure due to the high adhesion and elasticity of polyurethane.

To fabricate LIMBs, highly conductive graphene ink was firstly printed on the targeted substrates, e.g., polyethylene terephthalate (PET) and A4 paper, to form the interdigital current collectors, which can uniformly adhere onto the substrates and present high electrical conductivity ( $\approx$ 15 660 mS cm<sup>-1</sup>) (Figure S7, Supporting Information). After solidification, LFP@GC ink was precisely printed on one side of graphene-based current collector to obtain cathode, followed by printing LTO@GC ink on the opposite side to obtain anode (Figure 2a, Video S1, Supporting Information). As a result, the high resolution linear microelectrodes for LIMBs were clearly achieved



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**Figure 1.** Fabrication and rheological properties of LFP@GC and LTO@GC inks. a) Schematic of the components of LFP/LTO@GC and LFP/LTO@G inks. b) The photographs of "DICP" letter and c) corresponding SEM images of the printed LFP@GC, LTO@GC, LFP@G, and LTO@G inks, respectively. d,e) Storage modulus (G') and loss modulus (G'') as a function of shear stress for d) LFP@GC and LTO@GC inks, and e) LFP@G and LTO@G inks. f) Viscosities of LFP@GC, LTO@GC, LFP@G, and LTO@G inks as a function of shear rate.

(Figure 2b), and the multiple LTO@GC||LFP@GC-LIMBs can be obtained by screen printing one time (Figure S8, Supporting Information). Figure 2c shows various configurations of LIMBs printed on substrates of paper and PET, suggesting exceptional compatibility of the customized inks on various substrates. From cross-sectional SEM images, the one-layer printed microelectrodes of LTO@GC||LFP@GC-LIMBs showed a thickness of  $\approx$ 32 µm (Figure 2d,e).

The electrochemical performance of LTO@GC||LFP@GC-LIMBs was evaluated using an ionogel electrolyte of LiTFSI-P<sub>14</sub>TFSI-PVDF-HFP. For comparison, LTO@G||LFP@G-LIMBs were also fabricated with the similar procedure (see details in Experimental Section). Notably, LTO@GC||LFP@GC-LIMBs displayed high areal capacity of 131.4  $\mu$ Ah cm<sup>-2</sup> at a current density of 50  $\mu$ A cm<sup>-2</sup>, higher than LTO@G[|LFP@G-LIMBs (117.2  $\mu$ Ah cm<sup>-2</sup>). Moreover, LTO@GC||LFP@GC-LIMBs showed superior rate capability. For example, LTO@GC||LFP@GC-LIMBs printed one layer exhibited areal capacity of 131.4, 93.8, and 49.4  $\mu$ Ah cm<sup>-2</sup> at current densities of 50, 200, and 500  $\mu$ A cm<sup>-2</sup>, respectively. In a sharp contrast, LTO@G||LFP@G-LIMBs showed the low capacity of 117.2, 73.0, and 32.2  $\mu$ Ah cm<sup>-2</sup> at the corresponding current densities (Figure 2f). Apparently, it is observed that LTO@ GC||LFP@GC-LIMBs displayed higher voltage plateau and lower voltage polarization than LTO@G||LFP@G-LIMBs especially at a higher current density of 500  $\mu$ A cm<sup>-2</sup> (Figure 2g), suggesting that the 3D highly conductive framework of CNT and graphene in both LFP@GC and LTO@GC inks is beneficial for fast electron conduction and rapid lithium ion migration. This result was further demonstrated by the smaller electrochemical impedance (Figure S9, Supporting Information) and higher electrical conductivity (Figure S4, Supporting Information). Additionally, LTO@GC||LFP@GC-LIMBs retained a considerable capacity retention of 75.6% after 5000 cycles at 400  $\mu A$  cm^-2, demonstrative of extraordinary recyclability (Figure 2h).

In order to meet the demand of wearable electronics, it is a prerequisite for possessing excellent flexibility of the asfabricated micro-batteries. To this purpose, the electrochemical performance of printed LTO@GC||LFP@GC-LIMBs was tested under various torsion states. It can be seen that the mechanically stable microelectrodes of LIMBs with assistance www.advancedsciencenews.com

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**Figure 2.** Fabrication and electrochemical performance of LTO@GC||LFP@GC-LIMBs. a) Schematic of printable fabrication of multi-layer printed LTO@GC||LFP@GC-LIMBs. b) The interdigital LTO@GC||LFP@GC-LIMBs and enlarged images of microelectrodes patterns. c) Photograph of paperbased and PET-based printing microelectrode patterns consisting of different configuration. d,e) SEM images of cross-sectional LTO@GC||LFP@ GC-LIMBs. f) Rate capability and g) GCD profiles of LTO@GC||LFP@GC-LIMBs and LTO@G||LFP@G-LIMBs. h) Long-term cycling stability of LTO@ GC||LFP@GC-LIMBs.

of gel electrolyte acting as adhesive function displayed favorable integrity without any degradation or delamination (Figure 3a), showing strong adhesion of LFP@GC and LTO@GC inks to the PET substrate. The discharge capacity kept almost unchanged at 50, 80, and 200 µA cm<sup>-2</sup>, operating under considerable torsion, indicative of no local distortion of cracks in the microelectrodes (Figure 3b). Even when the devices were folded at different angles of 30°, 60°, 120°, 150°, and 180°, the capacity still remained unchanged at current densities of 80, 200, and 500  $\mu$ A cm<sup>-2</sup>, respectively (Figure 3c). The discharging profiles were almost overlapped at current densities of 80, 200, and 500  $\mu$ A cm<sup>-2</sup>, respectively, indicating excellent mechanical flexibility of printable LIMBs (Figure 3d). The capacity of LTO@GC||LFP@GC-LIMBs exhibited only an extremely small variation, with a retention of nearly 100%, when the microdevices were repeatedly bent for 7800 times (Figure 3e). Also, three-layer printed LTO@GC||LFP@GC-LIMBs showed

relatively stable performance after bending to 180° for 1000 times (Figure S10, Supporting Information). It is indicated that the LTO@GC||LFP@GC-LIMBs showed excellent flexibility without any breakage under random bending. Based on the superiority of the as-prepared inks, LTO@GC||LFP@GC-LIMBs with high areal loading of active materials were realized by multilayer printing approach, resulting in a remarkable improvement of discharge capacity to 398.1 µAh cm<sup>-2</sup> (50 µA cm<sup>-2</sup>) (Figure 3f) and relatively higher capacity retention of 76% after 3000 cycles for three-layer screen-printed electrodes, owing to the cross-linked network of graphene and CNT in the ink (Figure 3g). Through multi-layer printing of highly stable inks, our printed LIMBs simultaneously achieved high areal loading of conducting printed microelectrodes with outstanding electrochemical performance. It is noted that this discharge capacity was superior to the previous LIMBs (Figure S11, Supporting Information), such as 3D LTO || LiCoO<sub>2</sub> (LCO)-LIMB

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**Figure 3.** Flexibility and electrochemical performance of multiple-layer printed LTO@GC||LFP@GC-LIMBs. a) Photographs of flexible pack of LTO@GC||LFP@GC-LIMBs connected three cells in series at different torsion states. b) Discharge capacity of LTO@GC||LFP@GC-LIMBs obtained under different currents and torsion cycles. c) Discharge capacity and d) GCD profiles of LTO@GC||LFP@GC-LIMBs obtained under different currents and folding angles. e) Capacity retention of LTO@GC||LFP@GC-LIMBs under 7800 times bending. f) GCD profiles of LTO@GC||LFP@GC-LIMBs fabricated by screen printing 1 layer, 2 layers, and 3 layers. g) Long-term cycling stability of LTO@GC||LFP@GC-LIMBs printed in three layers.

(270 µAh cm<sup>-2</sup>),<sup>[40]</sup> 3D Li<sub>0.55</sub>La<sub>0.35</sub>TiO<sub>3</sub> (LLT) || LiMn<sub>2</sub>O<sub>4</sub> (LMO)-LIMB (32 µAh cm<sup>-2</sup>),<sup>[41]</sup> 3D carbon cloth-carbon nanofiber (CC-CF)@NiO || CC-CF@ZnO-LIMB (350 µAh cm<sup>-2</sup>),<sup>[42]</sup> and MXene@LTO || MXene@LFP-LIMB (88 µAh cm<sup>-2</sup>).<sup>[43]</sup> Further, considering the advantages of exceptional mechanical flexibility, cost-effectiveness and large-scale production, our screen printed LTO@GC||LFP@GC-LIMBs presented a highly competitive potential for planar microdevices in comparison with microbatteries fabricated by other technologies, e.g., 3D Printing<sup>[12,17]</sup> and mask-assisted filtration<sup>[25]</sup> (Table S1, Supporting Information). Impressively, the coulombic efficiency still maintained almost 100% after 4000 cycles for LTO@GC||LFP@GC-LIMBs printed twice at a current density of 400  $\mu$ A cm<sup>-2</sup> (Figure S12, Supporting Information), indicative of outstanding cycling stability. The GCD profiles of LTO@GC||LFP@GC-LIMBs printed from 1 layer to 3 layers at different current densities showed no obvious voltage drop (Figure S13, Supporting Information), which indicates that the multiplayer printing strategy is highly efficient for increasing areal capacity. Importantly, LTO@GC||LFP@GC-LIMBs with 1 layer printed electrodes

output a volumetric capacity of 41.0 mAh cm<sup>-3</sup> at 50  $\mu$ A cm<sup>-2</sup>, while the values were 61.5 and 62.2 mAh cm<sup>-3</sup> for two and three layers, respectively (Figure S14, Supporting Information). Moreover, there was almost no variation of volumetric capacity when LTO@GC||LFP@GC-LIMBs with two or more printed layers, suggestive of high electron-ion conductivity and mechanically stable structure of microelectrodes.

Benefiting from excellent mechanical flexibility and superior adhesion of the inks, LTO@GC||LFP@GC-LIMB showed ultrahigh areal energy density of 695  $\mu$ Wh cm<sup>-2</sup>, outperforming most previously reported micro-batteries, such as 3D LTO||LFP-LIMB,<sup>[12]</sup> 3D NiSn||LMO-LIMB,<sup>[44]</sup> 3D LTO||LCO-LIMB,<sup>[40]</sup> 3D LTT||LMO-LIMB<sup>[41]</sup> and 3D Li||LCO-LIMB<sup>[45]</sup> (Figure 4a). Correspondingly, the volumetric energy density of LTO@GC||LFP@GC-LIMBs is as high as 108.2 mWh cm<sup>-3</sup>, which is remarkably competitive to the representative values previously reported for flexible Zn||MnO<sub>2</sub> planar-MB (18.38 mWh cm<sup>-3</sup>),<sup>[46]</sup> LTO||LMO-LIB (48.09 mWh cm<sup>-3</sup>),<sup>[47]</sup> and commercial supercapacitor (SC) (0.58 mWh cm<sup>-3</sup>). Moreover, a high power density of 255.68 mW cm<sup>-3</sup> for LTO@GC||LFP@GC-LIMBs was obtained

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**Figure 4.** Comparison of energy density and power density of LTO@GC||LFP@GC-LIMBs with the reported energy storage devices. a) Comparison of areal energy density of LTO@GC||LFP@GC-LIMBs with various reported LIMBs. b) Ragone plot of LTO@GC||LFP@GC-LIMBs with other available energy storage devices (SC: supercapacitor).

(Figure 4b), which is two orders of magnitude higher than that of Li thin-film battery (5.53 mW  $\rm cm^{-3}).^{[48]}$ 

To further highlight the advantages of our customized ink, the various constellation micropatterns were printed on the PET substrate, where the shapes of these micropatterns presented high-resolution lines and zigzag angles (**Figure 5**a, Figure S15, Supporting Information). Based on the exceptional printability of the inks, LTO@GC||LFP@GC-LIMBs can be serially or parallelly connected through employing highly conductive graphene ink as metal-free interconnectors (Figure 5b,



**Figure 5.** Fabrication of fully designable printed constellations and a flexible wearable smart bracelet of LTO@GC||LFP@GC-LIMBs. a) Printed constellation by screen printing the customized inks. b) GCD profiles of LTO@GC||LFP@GC-LIMBs connected in series from one to two cells. c) A flexible and wearable smart bracelet by integrating a rechargeable LIMB, temperature sensor with LED. d) The conresponding schematic of intergrated circuit of the flexible intelligent bracelet, realizing temperature testing automatically. It can be possibly used for early prediction of novel coronavirus speedy. The inset in (d) is the photograph of the temperature sensor.



Figure S16, Supporting Information). Obviously, LTO@ GC||LFP@GC-LIMBs present proportional increase of the discharge capacity as increasing the number of parallelly connected cells, while the average plateau voltage keeps unchanged (Figure S16, Supporting Information). The serially connected LTO@GC||LFP@GC-LIMBs showed the multiplicative increase of output voltage while the capacity almost remains constant (Figure 5b), indicative of outstanding performance uniformity of printed LIMBs. Owing to the excellent integration character, an intelligent bracelet, composed of a serially-connected device, a temperature sensor and a LED, realized the detection of specific temperature. It is observed that, when the temperature is above 37 °C, the temperature sensor can efficiently detect the signal to bridge the integrated circuits, and subsequently the connected LED would be automatically turned on (Figure 5c). Based on this operating principle, this integrated intelligent bracelet system was also easily used for the detection of body temperature and further prediction for today's evil new-coronavirus (Figure 5d), demonstrative of wide applicability. Furthermore, our screen printed LIMBs with high areal mass loading still provide extraordinary mechanical flexibility, which is rarely reported previously. More importantly, a wearable smart bracelet, composed of a serially-connected LIMBs pack, a temperature sensor and a LED, automatically realized the detection of body temperature.

# 3. Conclusion

In summary, we have demonstrated the efficient fabrication of highly conductive and mechanically stable inks using polyurethane as a binder and introducing graphene and CNT as conductive additives to construct a 3D cross-linked conductive structure, which showed excellent rheological behavior for the customized planar LTO@GC||LFP@GC-LIMBs. The highly conductive screen-printed inks enabled the effective connection of insularly dispersed electrode particles for multiple-layer printed microelectrodes and sufficiently realized high electrical conductivity and long-range transport behavior of Li ions. Such excellent inks enabled the high-efficiency and scalable fabrication of flexible planar LTO@GC||LFP@GC-LIMBs with high areal loading of active materials in an extremely limited area, delivering remarkable areal energy density of 695  $\mu$ Wh cm<sup>-2</sup> and favorable cycling stability. Importantly, a wearable smart bracelet harnessing a rechargeable LIMB, temperature sensor and LED realized temperature testing for human. Therefore, this work will offer a novel insight into the exploitation of highly conductive and mechanically stable screen-printed inks for high areal energy density micro-batteries in wearable smart electronics.

### 4. Experimental Section

Preparation of LFP@GC and LTO@GC Inks: The highly conductive and stable inks of LFP@GC and LTO@GC were prepared by onestep ball-milling. To ensure uniformity and excellent adhesion of inks, polyurethane (Guangdong Wengjiang Chemical Reagent Co., Ltd.) was firstly dissolved in dibasic ester (Guangzhou jinshengji Chemical Co., Ltd.) to form a uniform adhesive solution (150 mg mL<sup>-1</sup>) under magnetic stirring for 12 h. Next, the LFP@G and LTO@G inks were obtained by adding electrode materials (e.g., LFP, or LTO), graphene and conductive super carbon (Tianjin An Nuohe New Energy Technology Co., Ltd.), with a weight ratio of 36:3:1 into the obtained binder solution, thoroughly mixing and ball milling for 5 h, in which the weight proportion of binder was about 14%. For comparison, the LFP@GC and LTO@GC inks were also prepared by the same procedure, using the mixture of CNT and graphene in the weight proportion of 1:1 instead of only graphene.

LTO@GC||LFP@GC-LIMBs: Fabrication of The printable LTO@GC||LFP@GC-LIMBs with an interdigital planar geometry (Figure S17, Supporting Information) were fabricated by screen printing the customized inks on flexible PET substrates. Firstly, the graphene ink, serving as current collectors, was initially printed with interdigital micropatterns. After vacuum drying at 60 °C, the LFP@GC ink was printed on one side of graphene current collector, while the other side of current collector was covered by LTO@GC ink. Furthermore, the highloading planar LIMBs were realized by repeatedly printing for three times and then vacuum dried at 80 °C. After that, an ionogel electrolyte of LiTFSI-P14TFSI-PVDF-HFP<sup>[25]</sup> was carefully coated on the printed electrode micropatterns. Finally, LTO@GC||LFP@GC-LIMBs were obtained. For comparison, the LTO@G||LFP@G-LIMBs using the same steps above were also fabricated without CNT additives.

Materials Characterization and Electrochemical Measurement: The morphology of the materials and electrode micropatterns was observed by SEM (JSM-7800F). The crystal structure of the materials (LFP and LTO) were characterized by XRD (SmartLab). The particle size distributions of LFP and LTO were carried out by micron laser particle size analyzer (Mastersizer 2000). The rheological properties of the inks were characterized by a rheometer (DHR2, TA Instruments-Waters LLC). Fourpoint probe equipment (RTS-9) was applied to evaluate the electrical conductivity of printed microelectrodes. GCD profiles were collected by a LAND battery tester (CT2001A) with the voltage between 1.0 and 2.5 V at current densities from 50 to 500  $\mu$ A cm<sup>-2</sup>. The electrochemical impedance spectroscopy (EIS) was tested from 100 kHz to 0.01 Hz with an AC amplitude of 5 mV in electrochemical workstation (CH1760E). The contact angle of water and ionogel electrolyte against different inks were conducted by contact angle measurements (KRUSS, DSA100).

The experiments of wearable smart bracelet placed on a wrist were carried out with the full, informed consent of the subject.

# **Supporting Information**

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

# Acknowledgements

Y.Z. and S.Z. contributed equally to this work. This work was financially supported by the National Key R@D Program of China (Grants 2016YFB0100100), the National Natural Science Foundation of China (Grants. 22075279, 22125903, 51872283, 21805273), the Liao Ning Revitalization Talents Program (Grant XLYC1807153), Liaoning BaiQianWan Talents Program, Dalian Innovation Support Plan for High Level Talents (2019RT09), The central government of Liaoning Province guides the funds for local science and technology development (Grant 2021JH6/10500112), Dalian National Laboratory For Clean Energy (DNL), CAS, DNL Cooperation Fund, CAS (DNL201912, DNL201915, DNL202016, DNL202019), DICP (DICP ZZBS201708, DICP ZZBS201708, DICP ZZBS201302, DICP I2020032), The Joint Fund of the Yulin University and the Dalian National Laboratory for Clean Energy (YLU-DNL Fund 2021002, 2021009), and China Postdoctoral Science Foundation (2019M661141, 2020M6809995).

# **Conflict of Interest**

The authors declare no conflict of interest.

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# Data Availability Statement

Research data are not shared.

# **Keywords**

flexible, ink, lithium ion micro-batteries, screen printing, we arable electronics

Received: September 12, 2021

Revised: September 29, 2021

Published online: November 27, 2021

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