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Conductive Inks Based on Lithium Titanate Nanotube Gel for High Rate Lithium-ion Batteries with Customized Configuration

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Development of high-performance lithium-ion batteries (LIBs) with ultrafast charging and discharging rates is highly demanded for portable/miniaturized electronic devices.^[1] Not only that, the advancement of these devices requires LIBs that are light, flexible, and can be miniaturized.^[2] From the materials perspective, it is important to develop electrode materials that are capable of ultrafast charging and discharging, as the rate capability of LIBs is kinetically limited by sluggish solid-state diffusion process in electrode materials.^[3] Meanwhile, electrode materials that can be solution-processed in large quantities are a prerequisite for the construction and customization of flexible or miniaturized electronics.^{[2c-e,}
^{4]} Furthermore, the development of solution-processable gel/ink material that is sprayable or printable possesses great potential for low-cost and large-scale industrial manufacturing.^[5] Driven by these demands, it would be highly desirable to develop solution-processable electrode materials inks with fast charging capability and to facilitate the construction of high-rate energy storage devices with customized configurations.

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is a promising material candidate for high-rate LIBs (> 10 C),

due to its fast Li-ion reaction kinetics based on an insertion-type mechanism.^[1h, 6] Its high lithiation voltage plateau (ca. 1.55 V vs. Li/Li⁺) and zero-strain volume expansion (~0.2% volume change) can avoid electrolyte decomposition and electrode structure distortion, respectively, thus endowing LIBs with long-cycling lives of over one thousand cycles.^[7] However, its rate performance is limited by large polarization at high charging rates, due to its low electronic conductivity (ca. 10⁻¹³ S cm⁻¹) and moderate ionic diffusivity (10⁻⁹-10⁻¹³ cm² S⁻¹).^[7b] Currently, although high rate LIBs performance (> 10 C) based on LTO electrode materials have been achieved through intrinsic materials engineering and electrode structure design, the development of solution-processable LTO precursor inks remains vastly difficult. Traditionally, LTO is synthesized by solid-state reaction (**Scheme 1a**), and intrinsic materials engineering of LTO^[6a, 7a, 8] (e.g., nanostructuring strategy, dopant manipulation and surface modification, etc.) relies on high temperature annealing (> 500 °C). The unstable thermodynamics during annealing results in severely aggregated nanostructures with random particle size distribution. This makes it difficult to re-disperse them in solvent to form a uniform ink, and the short length of the individual nanostructures hinders them from linking together to form a continuous conductive network electrode for high-rate LIBs application.^[1c]

^{9]} Alternatively, LTO nanostructures (tubes, wires, nanosheets, etc.) can be grown directly on titanium substrates, yielding LIBs with superior high-rate performance (> 100 mAh g⁻¹) at more than 100 C.^[10] More recently, LTO materials with patterned current collectors can significantly enhance rate capabilities and cycling retention, and the patterned full cell battery based on LiFePO₄ and LTO exhibited ca. 70 mAh g⁻¹ during 1000 cycles at 10 C.^[11] However, the above two methods rely on the use of metal substrates, which may not be suitable for the customized LIBs application, e.g. large scale electrode processing, or miniaturized electronics fabrication. These limitations have strongly motivated us to develop solution-processable gel or ink based on lithium titanate with conductive network architecture, which is capable of fast charging.

According to the Flory's definition,^[12] a gel system is composited of a continuous structure with macroscopic dimensions within colloidal dispersion. The continuous structure is solid-like in its rheological behaviour and is stable with time.^[5a] Inspired by this, we develop a conductive gel system that comprises a continuously conductive LTO network based on cross-linking lithium titanate nanotubes (Li-TNT) hydrogel and graphene oxide (GO) colloids, in order to achieve high-rate LIBs. Herein, the conductive gel was rationally designed in order to meet the criteria for gel formulation.^[2b, 2c, 12-13] Firstly, our gel possesses a tunable viscosity via tuning the hydrogel concentration to make it compatible on demand for various coating techniques, including spraying, drop casting, and screen-printing techniques (Figure S1). Benefited from this, the LIBs with customized configuration (coin cell, pouch cell, or on-chip miniaturized device) are achieved in this work. Secondly, the gel remains stable without aggregation via the electrostatic repulsion effect. The electrode synthesized through this conductive ink meets the requirements^[1c, 1h, 14] for high-rate LIBs: (1) enhanced electron transport due to the highly continuously conductive network (ca. 1.0 S cm^{-1}) of reduced GO (RGO) nanosheets; (2) short diffusion length of Li^+ ion and high ionic conductivity (ca. $3.6 \times 10^{-12} \text{ cm}^2 \text{ S}^{-1}$) for fast ionic transport; and (3) an interconnected porous nanotube network which served as Li^+ ion reservoirs for speeding up ion transport across the entire film. As expected, the proof-of-concept coin-cell LIBs exhibited excellent high-rate performance (ca. 124 mAh g^{-1} at 90°C , 15.7 A g^{-1}) after 1000 cycles, as well as for pouch cell and on-chip miniaturized LIBs. The protocol of producing LTO inks through solution-processing will open up enormous opportunities for manufacturing inks of other electrode materials for high-performance energy storage devices.

The conductive inks composed of cross-linking nanotubes and well-dispersed GO nanosheets were prepared as follows (Scheme 1b). Firstly, the anti-aggregation sodium-titanate elongated nanotube gel was fabricated by a stirring hydrothermal reaction.^[14] Next, the sample was subjected to a Li^+ ion-exchange process to obtain Li-TNT gel (**Figure 1a**), in

which the original Na^+ ions were fully replaced by Li^+ ions, as can be seen from the energy-dispersive X-ray (EDX) spectrum in Figure S2. To make the Li-TNT gel conductive, GO nanosheets were added as the conductive linker as they possess excellent solubility in organic solvents and high electronic conductivity after the reduction process.^[15] Also, GO nanosheets are feasible to build the binder-free electrode since they can spread and adhere well on the current collector due to high van der Waals attraction and large contacting surface area.^[15]

The surface charge control (Figure S3) of both Li-TNT and GO in ethanol was extremely important; both needed to possess negative charges by using electrostatic repulsion to prevent their aggregation or serious stacking of GO sheets, thus enabling them to mix well and form a homogeneous ink (Figure 1a). Moreover, the viscosity of conductive inks is tunable through changing the ink concentration in ethanol (see Supporting Information). In a typical spraying process, the obtained ink (5 mg/mL) was sprayed on copper foil on the hotplate with the temperature ca. 80 °C using the spray pistol. The fast drying process of volatile solvent system ensured the instant solidification and adhesion of inks on the copper foil, warranting the structure integrity. After drying, the ink was homogeneously spread and adhered well to copper foil (Figure S1 & Scheme 1b). This could be attributed to the unique cross-linking elongated nanotubular structure, which enabled the Li-TNT to form a continuous networking electrode (Figure S4) without the addition of binder. After thermal annealing in vacuum, Li-TNT precursor was mainly transformed into crystalline LTO with a small fraction of anatase TiO_2 (Figure 1b). Meanwhile, the successful reduction of GO to RGO was confirmed by the observation of an increase of D/G intensity ratio through Raman spectroscopy (Figure 1c).^[15k]

During the vacuum annealing, the thermally unstable oxygen functionalities (residual carboxyl and carboxylates groups, etc.) are removed in the form of water, carbon dioxide, and carbon monoxide while the sp^2 carbon network structure is restored.^[15m] This reduction process is also confirmed by X-ray photoelectron spectroscopy (XPS, Figure S5) since the intensities of respective peaks for C-O bonds, C=O bonds and O-C=O bonds are reduced. As

expected, the percentage of deoxidized carbon (C-C) is estimated to be 84% for RGO, which is much higher than the value (62%) estimated for the pristine GO. The ability of the elongated nanotubular structures to withstand aggregation is proved despite heat-treatment (Figure 1d), and the RGO nanosheets were uniformly distributed on the nanotube surface. The transmission electron microscopy (TEM) images showed the evident formation of hollow nanotubular structure with an inner pore size of 2~5 nm (Figure 1f), and the intimate contact between the LTO nanotubes bundles with the RGO nanosheets (Figure 1e-f). High-resolution TEM revealed the formation of multi-layered RGO nanosheets with an interlayer distance of 0.38 nm (Figure 1g), and a lattice fringe of 0.22 nm that is the characteristic of (222) planes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Figure 1h). To gain further insight into LTO/RGO hybrid nanostructures, scanning transmission electron microscopy (STEM)-EDX elemental mapping was conducted. As seen in Figure 1i-m, carbon, titanium and oxygen atoms were homogeneously distributed in LTO/RGO samples. These results clearly showed that the LTO nanotubes were well linked with RGO nanosheets, which enhanced the conductivity of the LTO/RGO sample. Based on the aforementioned results, we predicted that the LTO/RGO hybrids may be an excellent electrode materials candidate for high-rate LIBs.

As a proof-of-concept, the performance of the binder-free LTO/RGO hybrids as anode electrodes was evaluated. The electrodes exhibited minor discharge capacity decrease from 216 to 125 mAh g^{-1} at stable state (**Figure 2a-b**) as current rate increases from C/5 to 90 C (1 C = 175 mA g^{-1}). The capacity returned to 208 mAh g^{-1} at C/5, and almost 96% of the initial capacity at C/5 was maintained. This is in contrast to the pure LTO sample and RGO samples, the rate performances of which dramatically decreased to 4 and 2 mAh g^{-1} at 90 C, respectively. The low capacity of RGO was due to the fact that the reaction potential (1-3 V) is far from its lithiation windows. These results confirmed the synergic effect between RGO and LTO in the LTO/RGO system towards achieving such outstanding high-rate performance, and the RGO predominantly functioned as conductive electrons highway for LTO nanotube.

As a result, the low lithiation/delithiation potential separation is observed (Figure 2b) even at high rate. Although the cell voltage decreases slightly with the increasing current density, it still shows a nearly flat potential plateau at 0.2-30 C, indicating the fast lithiation kinetic during two-phase reaction. The redox reaction peaks revealed that the intercalation storage behavior arose from the LTO (1.55 V vs. Li/Li⁺) and TiO₂ (1.75 V vs. Li/Li⁺) nanotubular electrodes (Figure 2c), which was consistent with the XRD result (Figure 1b). Impressively, the electrode displayed capacitive-like charge storage behaviour,^[16] a nearly constant slope of galvanostatic (current-potential) characteristic was observed at 90 C, indicating ultrafast kinetics during lithiation/de-lithiation process. The LTO/RGO electrode demonstrated long-term cycling performance at 90 C (Figure 2d), and it also retained 95% of its initial capacity (130 mAh g⁻¹) after 1000 cycles with almost 100% Columbic efficiency.

To understand the ultrafast electrochemical kinetics of LTO/RGO hybrids, we studied the intrinsic materials property and dynamic ionic/electronic measurement at each charging/discharging state (Figure 2e-g). It was revealed that the introduction of RGO sheets into the LTO nanotube led to the improved electronic conductivity and Li⁺ ion diffusion compared with bare LTO nanotube electrode (Figure S6a). Using the four-point probe method, we proved that the electronic conductivity of LTO/RGO (ca. 1.0 S cm⁻¹) was more than 4 orders of magnitude higher than that of the LTO electrode (ca. 2.3×10⁻⁵ S cm⁻¹). In-situ electrochemical impedance spectroscopy (EIS) study was conducted to probe the electronic behavior of LTO/RGO materials during lithiation/delithiation process. As shown in Figure S6b-c, the Nyquist plot consisted of a high frequency depressed semicircle and a linear Warburg region. The high-frequency semicircle is characteristic of cell internal resistance (R_s) and the diameter of the depressed semicircles is the charge transfer resistance (R_{ct}), while the oblique line at low frequencies represents the Li⁺ ion diffusion process in electrode materials.^[8d] The correlation of R_{ct} and R_s with each charging or discharging state was plotted as shown in Figure 2f. It was found that R_s is small and showed minor differences (4.2 ± 0.1

Ω , Figure 2f) at each charging and discharging state. For R_{ct} , an initial minor increase and subsequent continuous decrease could be observed during the lithiation process from 2.1 (47.5 Ω) to 1.0 V (39.5 Ω) (detailed discussion in note of Supporting Information). The decrease of R_{ct} is due to the reduction of Ti^{4+} into Ti^{3+} , which resulted in the improvement of the conductivity.^[7d, 17] During the delithiation reaction, the charge transfer resistance increased first and then slightly decreased to 47.4 Ω at 2.1 V, which was closed to the initial state. The low R_s change and stable R_{ct} transition suggested that the lithiation/delithiation process in the LTO/RGO hybrid was completely reversible without by-reaction, which was highly beneficial for electron conduction. In addition, it was found that oxygen vacancies were generated in the LTO/RGO nanotubes annealed in vacuum, as Ti^{3+} characteristic peaks (Figure S7) were observed. It has proven that the surface conductive Ti^{3+} -doped LTO can facilitate the electrons transport within the electrode,^[8h, 10a] which is also beneficial for high-rate LIBs.

Apart from electronic conductivity, the as-prepared LTO/RGO hybrid also showed the improvement in ionic conductivity compared to that of the LTO electrode (Figure S6a). The Li^+ ion diffusion coefficient D_{Li^+} ($cm^2 S^{-1}$) for LTO/RGO can be calculated from the Nyquist plots in low-frequency according to the following equations:^[18]

$$Z_{re} = R_{ct} + R_s + \sigma\omega^{-1/2} \quad (1)$$

$$D_{Li^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (2)$$

where R is the gas constant, T is the absolute temperature, n is the total number of electron transferred, ω is angular frequency, F refers to Faraday constant, and A is the area of electrode/electrolyte interfaces. From Eq. (2), the evolution of D_{Li^+} of the LTO/RGO electrode (Figure 2g) was calculated at each discharging state from the $Z_{re} - \omega^{-0.5}$ plots in Figure S8. It is clear that D_{Li^+} increased steeply upon the insertion of Li^+ ion into LTO at the early stages, which stemmed from the generation of strong repulsive Coulomb interactions because of the simultaneous occupation of (face-sharing) 8a and 16c sites within the spinel

structure of LTO.^[19] This is associated with a significant reduction of the mean activation barrier. In the two-phase equilibrium region of LTO and $\text{Li}_7\text{Ti}_5\text{O}_{12}$, D_{Li^+} was slowed down due to the increase of activation barrier for the end product of rock-salt type $\text{Li}_7\text{Ti}_5\text{O}_{12}$. After charging, the value of D_{Li^+} could go back to its initial state like the R_{ct} . In conclusion, in-situ EIS study revealed that the LTO/RGO hybrid exhibited low electronic resistance dynamic change and high ion diffusion coefficient at different charging states, which is critical for reducing the electrode polarization and ionic diffusion energy barrier for high-rate LIBs.

To gain electrochemistry insight on the reaction kinetics of LTO/RGO, cyclic voltammetry (CV) was conducted with a scan rate from 0.1 to 200 mV/s (**Figure 3a**). It is interesting to note that anodic/cathodic peak separation is small (ca. 80 mV at 0.1 mV/s) when the scan rate increased from 0.1 to 5 mV/s (inset of Figure 3a), suggesting low polarization at high scan rates. In general, the CV current (i) is related to scan rate (v) by the equation:^[20]

$$i = av^b \quad (3)$$

The b -value can be determined by the slope of the $\log(v)$ - $\log(i)$ plots (Figure 3b). A b -value of 0.5 indicates rigorous diffusion behavior, whereas the value of 1.0 suggests a capacitive process.^[20] In this work, the b -value of the LTO/RGO electrode was 0.65 for a wide range of scan rates from 0.1 to 100 mV/s (180 C, Figure 3b), which indicated that the Li^+ ion could rapidly insert/de-insert into LTO/RGO electrode even at ultrahigh rates. As the b -value was higher than 0.5, this indicated mixed contribution from both capacitive surface storage and diffusion controlled reaction, which is benefited from high conductive RGO nanosheets.^[1c, 20-21] This is different from the pure LTO electrode (Figure S9), in which the two slopes were separated at 1 mV/s, thus reflecting a decrease in b -value from 0.45 (< 1 mV/s) to 0.37 (> 1 mV/s) due to low diffusion kinetics as well as large polarization at ultrafast scan rates. Here, we can divide the total charge (q_{total}) of the electrode materials into:

$$q_{total} = q_{surface} + q_{bulk} \quad (4)$$

$$q_{bulk} = n \rho F A \sqrt{\frac{2 D_{Li^+} \Delta V}{\nu}} \quad (5)$$

$$l = \sqrt{2 D_{Li^+} t} \quad (6)$$

where $q_{surface}$ is surface capacitive charge, q_{bulk} is diffusion reaction charge, n is stoichiometric number of electrons consumed in the electrochemical reaction; ρ is the Li^+ ion density in the bulk electrochemical reaction sites; and F , A , ΔV , ν , l , and t are the Faraday constant, diffusion area, potential range, scan rate, diffusion length and diffusion time, respectively. The plots of $\nu^{-0.5}$ versus voltammetric charges (q_{total} , Figure 3c) shows two linear ranges (Figure S9e), and q_{total} was integrated from the plot of i vs. t (as a function of scan rate) derived from Figure 3a. Since surface capacitive reaction ($q_{surface}$) is faster than diffusion reaction (q_{bulk}), the total charge loss (q_{total}) was mainly due to the decrease in bulk diffusion reaction at high scan rates. The slope at low scan rate (< 1 mV/s) was small and q_{total} was close to the theoretical value, which suggested that full Li^+ ion diffusion into the LTO/RGO and LTO electrodes occur without kinetic limitations at low scan rate (< 1 mV/s, 1.8 C, Figure S9e). At high scan rates (1-100 mV/s, 1.8-180 C), the charge loss of LTO/RGO was lower than that of LTO, which means that bulk charge storage is predominant in the LTO/RGO electrode. However, at extremely high scan rates (100-500 mV/s, 180-900 C), a sharp linear drop of q_{total} for both electrodes were observed due to the rate-limited diffusion reaction (q_{bulk}). The magnitude of the q_{total} drop was greater for the LTO electrode (5 C/g) than that of the LTO/RGO electrode (119 C/g, 500 mV/s) (Figure 3c). This kinetic study is consistent with the rate-dependent electrochemical performance of LTO/RGO and LTO in Figure 2.

Herein, we have successfully achieved remarkable high-rate battery performance, which can be attributed to the following two key characteristics: high electron conductive network and fast Li^+ ion diffusion kinetics. The 3D RGO network functioned as the conductive highway that enabled the fast transport of electrons from current collector to LTO nanotube surface (Figure 3f). This is beneficial towards achieving low internal resistance (4.2

$\pm 0.1 \Omega$) and charge-transfer resistance ($< 50 \Omega$) during the charging/discharging process. In basic electrochemistry (Eq. 5), the performance of high-rate LIBs (q_{bulk}) is determined by the D_{Li^+} and area of surface reaction sites (A). We have confirmed that the Li^+ ions diffusion kinetics inside the LTO/RGO electrode is faster than that of the LTO electrode (Figure S6a). This can be attributed to the following key merits. Firstly, the interconnected porous electrode served as Li^+ ion reservoirs for fast Li^+ ion transport (Figure 3f). The LTO/RGO hybrid possesses a surface area of around $51 \text{ m}^2/\text{g}$ (Figure 3d), which is higher than literature reported lithium titanate synthesized through the traditional solid-state method ($< 5 \text{ m}^2/\text{g}$).^[8h] The gaps between the thin RGO nanosheets and LTO nanotubes clearly contribute to the mesoporosity of the hybrids, with the inner diameter of the LTO nanotube constituting a narrow pore size distribution with a peak value of 3.2 nm (inset in Figure 3d). Secondly, the penetrable structure of the LTO/RGO electrode is favorable towards the flow and exchange of electrolytes. The wettability of LTO/RGO electrode allows the electrolyte to perpetrate the thin film within 1 s (Figure 3e) with a contact angle of zero degree. Thirdly, the short diffusion length (l) of Li^+ ion (Figure 3g, Eq. 6) into the LTO nanotube reduces the Li^+ diffusion time. Geometrical calculations (note in Supporting Information)^[9d] revealed that the average thickness (h) of the nanotube is around 12 nm . According to Eq. (3), the characteristic diffusion time is less than 1.0 second along the lateral direction, thus enabling fast Li^+ ion insertion/de-insertion. Indeed, the Li^+ ion can rapidly insert/de-insert into the LTO/RGO electrode even at the high scan rate of 100 mV/s (180 C , Figure 3c). The above kinetic studies provide convincing evidence of the high-rate capability of our LTO/RGO electrodes.

To prove the viability of preparing our LTO/RGO electrodes by the facile spraying technique, we prepared large scale flexible pouch cells with commercial $LiFePO_4$ as the cathode (Figure S10-11), in order to further investigate its electrochemical properties. **Figure 4a** shows the cycling performance of the full cells at 0.2 C ($1 \text{ C} = 175 \text{ mA g}^{-1}$). After 100

cycles, the full cells can maintain 84% (152 mAh g^{-1}) of their initial discharge capacity, giving a Coulombic efficiency of 98%. The low potential hysteresis between the charge/discharge profiles (Figure 4b) is observed, indicating excellent conductivity and fast reaction kinetics of electrode. Figure 4c shows that the discharge capacity decreases slightly from 151 mAh g^{-1} to 140, 130, 105 and 89 mAh g^{-1} as the current rate increases from 0.5 C to 1, 2, 5 and 10 C, respectively. Furthermore, the capacity can return to 143 mAh g^{-1} when the current rate was returned to 0.5 C, thus retaining 95% of its initial capacity. The high-rate performance of our battery is better than that of the full cell battery made of the commercial LTO and LiFePO_4 electrode materials (Figure S12), but it is lower than that of the half-cell LTO/RGO electrode, due to limitations arising from the microscale particle sizes of the commercial LiFePO_4 cathode (Figure S10). After fast charging at 10 C, the obtained pouch-type battery cell is capable of strongly powering 38 LED lamps (Figure 4d). This proves that the as-prepared LTO/RGO hybrid can serve as an outstanding high-rate anode material for full cell LIBs.

Beyond the spraying technique, we have also demonstrated the possibility of using screen printing method to fabricate on-chip miniaturized full-cell LIBs (Figure 5a). The millimeter-sized electrode was prepared by screen printing of the conductive lithium titanate nanotube gel and LiFePO_4 inks on a 3D printing electrode pattern (detailed information in experimental section), and then the cell was sealed with a PDMS case to encapsulate battery electrodes and liquid electrolyte. It is observed that the uniformly distributed LiFePO_4 nanoparticles (obtained after centrifuge separation) with an average diameter of ca. 200 nm are enwrapped with gauze-like GO nanosheets in large scale (Figure 5b, Figure S13a-b), which adhere well on conductive gold substrate. The morphology of LTO/RGO anode electrode (Figure 5c, Figure S13c-d) is similar to the previous results (Figure 1) on the copper substrates. As shown in Figure 5d, the cell shows stable reduction peaks (at 1.2 V & 1.7 V) and oxidation peaks (at 2.1 V) at the scan rate of 5 mV s^{-1} (Figure 5d), and another oxidation peak at 1.8 V (lithiation in anatase) is obvious at low scan rate of 0.5 mV s^{-1} (Figure S14a).

This is consistent to electrochemical characterization on full cell LIBs (Figure 4b, Figure S11b). After CV measurements, galvanostatic charge and discharge at high rate was conducted, and the lithiation/de-lithiation plateau related to fast lithium ion insertion process was also observed (Figure S14b). For example, the discharge capacity of the packaged on-chip battery cell is ca. 1.4 and 0.5 $\mu\text{Ah}/\text{cm}^2 \cdot \mu\text{m}$ at 13 C (Figure S15) and 36 C (Figure 5e-f) respectively, and the cell device demonstrates the stable electrochemical performance with slight deviation after 50 cycles. The packaged battery does not exhibit long-term cyclability due to lack of hermeticity since the liquid electrolyte is found to be unstable (evaporation, reacted with glue or PDMS, etc.) in PDMS case after several hours, and the stable package of on-chip miniaturized batteries is quite challenging up to date.^[2c-d] Moreover, the capacity bias between charging and discharging process may be due to the minor leakage of electricity resulted from the packaging issues, which is also observed in the previous work for microbattery cell.^[2c] Herein, we have demonstrated the proof-of-concept miniaturized LIBs by using lithium titanate nanotube gel and $\text{LiFePO}_4/\text{GO}$ nanosheet ink, and the device have exhibited the fast rechargeable capability. Although the area capacity is lower than the reported micro-battery,^[2, 4] the further performance optimization of miniaturized LIBs using nanoscale cathode materials with porous structures, electrode architecture design (width, gap distance of electrode line) as well as battery packaging is currently under investigation.

In summary, we developed solution-processable inks based on lithium titanate with conductive network architecture, for application in high-rate LIBs. The ink formation procedure is simple and high-yielding, and the ink's tunable viscosity renders it compatible for various on-demand coating techniques, such as spraying, drop casting, and screen-printing. The proof-of-concept LTO/RGO electrode enabled the construction of a long-lifetime LIBs with supercapacitor-like rate performance and battery-like capacity, which can be attributed to two key characteristics: highly electron conductive network and fast lithium ion diffusion kinetics. The former is due to the continuously conductive reduced graphene oxide

nanosheets, which served as the conductor component to bridge the conduction between the LTO nanotubes and the current collector. The latter is due to the intrinsic high lithium ion diffusion coefficient, short solid-state diffusion length, and mesoporous nanotube network of LTO electrode, which can speed up the ion transport across the entire film to shorten the diffusion time. This fundamental understanding would be extremely useful in the development of customized energy storage devices with high-rate capability.

Supporting Information

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

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Scheme 1. Schematic illustration of the synthesis of conductive lithium titanate nanotube (Li-TNT) inks. (a) The traditional solid-state method of fabricating LTO: (1) mixing a lithium oxide compound (LiOH , Li_2O , etc.) with TiO_2 -based particles or one-dimensional nanotubes/nanowires; (2) followed by high-temperature annealing process. The obtained final product tends to aggregate severely under solid-state reaction. (b) Our approach on the in-situ formation of conductive Li-TNT inks: (i) ion-exchange process to obtain Li-TNT precursor; (ii) spraying technique to obtain uniform conductive Li-TNT precursor on Cu foil, which would convert to LTO/RGO after thermal treatment (digital photo). Schematic illustration of (c) the screen-printing process and (d) the drop-casting process of the conductive Li-TNT inks.

Figure 1. Material characterization of the conductive Li-TNT inks and the RGO/LTO nanohybrids after vacuum thermal treatment: (a) Digital photograph of the as-prepared Li-TNT/GO (left) and Li-TNT (right) inks; (b) XRD pattern of the obtained LTO/RGO after thermal treatment (the pound symbol indicates the trace of anatase TiO_2); (c) Raman spectra of Li-TNT/GO (olive) and LTO/RGO (purple) after thermal treatment; (d) FESEM image of the LTO/RGO electrode; (e-f) TEM image of LTO/RGO nanohybrids showing their homogeneous combination; (g-h) High-resolution TEM image of the (g) RGO and (h) LTO component in the LTO/RGO hybrid; (i) STEM image and corresponding EDX spectrum (j) as well as EDX maps of (k) carbon, (l) titanium and (m) oxygen in the LTO/RGO sample.

Figure 2. Electrochemical performance and in-situ electrochemical impedance spectroscopy (EIS) study of the binder-free LTO/RGO samples. (a) Rate performance of the RGO, LTO, LTO/RGO hybrids; (b) Discharge curves at different current rates of C/5 ~ 90 C; (c) The first 10 consecutive cycles of CV curves at a scan rate of 0.1 mV s⁻¹; and (d) Long-term cycling performance at a high current density of 90 C, showing the reversible capacity value of 125 mAh g⁻¹ after 1000 cycles with Coulombic efficiency of ca. 100%. The Coulombic efficiency is plotted on the right axis of b and f (blue circles). In-situ EIS measurement of LTO/RGO electrode: (e) Discharging and charging potential profiles; (f) The evolution of internal resistance (R_s), charge-transfer resistance (R_{ct}), and (g) Li⁺ ion diffusion coefficient (D_{Li^+}) of the LTO/RGO electrodes at different charging and discharging states.

Figure 3. Electrochemical kinetic analysis and intrinsic property of the LTO/RGO electrode. (a) CV curves at various scan rates from 0.1 to 200 mV/s; the insets in (a) are the CV curves at a scan rate of 0.1 mV/s (left) and the narrow scan range of 0.1-5 mV/s (right). (b) The relationship between peak current and scan rate for the determination of b -value. (c) Voltammetric charge (q) as a function of $v^{-1/2}$ for the LTO/RGO and LTO samples. (d) Isothermal nitrogen sorption of the LTO/RGO sample and the inset in (d) shows its pore volume distribution (BJH desorption); (e) Optical images of a battery electrolyte droplet on the surface of the LTO/RGO sample electrode at 0, 0.5 and 1 s after dropping on to the electrode surface. Schematic illustration of (f) the 3D conductive LTO network electrode for the ultrafast charging and discharging and (g) the electron and Li⁺ transport pathways in the individual nanotube and RGO nanosheet.

Figure 4. Electrochemical performance of the full cells assembled with LTO/RGO as the anode and commercial LiFePO_4 as the cathode. (a) Specific capacity and Coulombic efficiency of full cell battery for 100 cycles at a current density of 0.2 C ($1 \text{ C} = 175 \text{ mA g}^{-1}$); (b) The capacity versus voltage curves of the full cell at 0.2 C; (c) The rate performance and Coulombic efficiency of the full cell; (d) The capability of the full-cell battery in powering 38 LED lamps (inset photo is taken under the dark condition). The Coulombic efficiency is plotted on the right axis of b and d (blue circles).

Figure 5. (a) Schematic of on-chip miniaturized full cell LIBs composed of LTO/RGO (anode) and commercial LiFePO₄ (cathode)/RGO after the packaging. (b) Photos of the cathode inks made of LiFePO₄ nanoparticles and GO nanosheets, and the corresponding FESEM image of LiFePO₄/RGO (cathode) electrode after annealing. (c) Photos of the anode inks made of lithium titanate nanotube and GO nanosheets, and the corresponding FESEM image of LTO/RGO (anode) electrode after annealing. (d) Cyclic voltammetry of the packaged on chip LIBs at scan rate of 5 mV/s. The A and B reduced peaks are attributed to the extraction of lithium ion from Li₄Ti₅O₁₂ and anatase TiO₂ respectively. (e) Cyclic performance and (f) its corresponding charge/discharge curves of on-chip miniaturized LIBs with cycle number at a charging rate of ca. 36 C. The inset in (e) is optical image of the on-chip miniaturized full cell LIBs.

The table of contents entry

We developed solution-processable inks based on lithium titanate with conductive network architecture towards high-rate LIBs with customized configuration, and the inks with tunable viscosity are compatible for on-demand coating techniques. The lithium titanate electrode derived from these inks exhibited excellent high-rate capacity (ca. 124 mAh g⁻¹ at 90 C, 15.7 A g⁻¹) after 1000 cycles.

Keyword: High-rate charging, lithium-ion batteries, conductive inks, sprayable coating, lithium titanate nanotube

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Conductive Inks Based on Lithium Titanate Nanotube Gel for High Rate Lithium-ion Batteries with Customized Configuration

TOC Figure