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Advanced Cu-free Bipolar Solid-state Lithium-ion Battery Promoted by Li⁺ Conductive Matrix Enabled Excellent Iron Oxide Anode

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Abstract

Bipolar lithium-ion batteries (*b*-LIBs) with internal series configuration possess great advantages in conversion rate from theoretical energy density to practical values when compared with classic ones. Herein, advanced Cu-free *b*-LIBs with further simplified structure can be achieved by utilizing an amorphous Li⁺ conductive Li-Fe-BO₂ matrix enabled iron oxide anode (FeO_x-LFBO) with intermediate cutoff voltage (≥ 0.5 V) beyond lithiation potential of Al foil. The rational designed LFBO matrix can serve as a Li⁺ conductor/reservoir to enable fast Li⁺ diffusion, a heterogeneous nano-reactor to interdict aggregation of Fe + Li₂O precipitates, a binder to aggregate particles, and a soft buffer to remit volume change. The FeO_x-LFBO has a high tap density of 1.6 g cm⁻³, good electronic conductivity, and high Li⁺ conductivity. As an anode the intermediate cutoff voltage of 0.5 V, it harvests the admirable capacity of 710 mA h g⁻¹

at 0.5 A g⁻¹, excellent cycling stability (95% after 1000 cycles), and capacitive rate capability (192 mA h g⁻¹ at 50 A g⁻¹). Such an excellent anode is assembled into a novel Cu-free LIB, delivering an ultra-high energy density of ~350 Wh kg⁻¹, outstanding power density of ~6700 W kg⁻¹, and long-term cycling stability (75% after 2000 cycles), much better than state-of-the-art Li₄Ti₅O₁₂ battery (≤100 Wh kg⁻¹, ≤5000 W kg⁻¹). Moreover, a Cu-free solid-state bipolar pouch cell is also fabricated successfully with high voltage of 7.6 V, great cycling stability, and safety. This study may set off an upsurge in studying intermediate cut-off voltage anodes and novel *b*-LIBs in the future.

Introduction

Lithium-ion batteries (LIBs) have undergone countless improvements in cell configurations and electrode materials since been commercialized in 1991. Actually, the optimization of the cell configuration has played a crucial role for the higher energy density, higher power density, longer lifetime, better safety, and lower cost.¹ For instance, despite of using identical LiCoO₂ cathode and graphite anode, the engineers have successfully increased the energy density of such a LIB to 200 Wh kg⁻¹ from an initial 80 Wh kg⁻¹ through substantial optimizations in cell configurations.² Bipolar lithium-ion batteries (*b*-LIBs) possess an advanced stack configuration that ultimately simplifies the cell components and thus may arouse the next battery industry revolution.

As shown in **Figure 1A**, in *b*-LIBs, cathode and anode slurries are separately coated on both sides of the same current collector, whose each units (unit number $n \geq 2$) are internal series connected other than external series of classic LIBs

(**Figure S1**). Therefore, *b*-LIBs are more competitive in the application of electric vehicles while these electrified transportations need for the battery packs with working voltage of 300–500 V.³ Detailed cell configurations and attempts have been performed in recent years. For example, the cathode and Li metal anode were coated on one side of internal series connected Al and Cu foils to fabricate a solid-state *b*-LIBs.⁴ To avoid the Li-alloying of Al foils at low potentials (~ 0.3 V) and the oxidization of Cu foils at high potentials (> 3.5 V), stainless steel was utilized as the current collector to achieve a workable *b*-LIBs.⁵ Regrettably, when compared with Al foil, stainless steel still has the disadvantages of high-voltage resistance, thickness, density, electronic conductivity, and cost. The Al foils designed for both cathode and anode are capable only if the anodes are replaced to high/intermediate cutoff voltage materials, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ⁶⁻⁸ and $2,6\text{-Naph}(\text{COOLi})_2$ ⁹.

To the best of our knowledge, ideal *b*-LIBs (**Figure 1A**) should be designed by the following three points: (1) Traditional liquid electrolyte should be replaced to solid-state electrolyte to avoid short circuit between cathode and anode on the two sides of the same Al foil; (2) Single current collector should be applied to give full play to *b*-LIBs' advantages, while the most promising candidate is Al foil; (3) Anode materials with the intermediate cutoff voltage (≥ 0.5 V) and high capacity beyond $\text{Li}_4\text{Ti}_5\text{O}_{12}$ should be well developed to satisfy point (2). Benefit from such design, three fascinating advantages of *b*-LIBs are: (1) a simple and compact design for higher energy density; (2) a high-voltage and current output

for higher power density; (3) a short electron transfer for a homogeneous current distribution and lower ohmic resistance for greatly reduced heat production.¹ Detailed comparison between LIBs and *b*-LIBs is shown in **Figure 1B**, where *b*-LIBs take advantages in almost all aspects except technology maturity.

Figure 1. Comparison of classic LIBs and *b*-LIBs. (A) Schematic images of ideal solid-state bipolar LIBs. (B) Spider diagram to show the properties of LIBs and *b*-LIBs. (C) Conversion rate from theoretical gravimetric energy density to practical values. (D) Average charge voltage of anode and energy density based on anode and cathode (Wh kg^{-1}) vs. anode capacity with the cutoff voltage ≥ 0.5 V. Cathode is assumed to be 4.6 V LiCoO_2 with specific capacity of 210 mA h g^{-1} with the average potential of 4.0 V vs. Li/Li^+ . Inset: Typical CV curves of Fe_2O_3 anode.

Among these advantages, *b*-LIBs harvest inspiring enhancement when evaluating the practical energy density from theoretical values at cell or system level, as shown in **Figure 1C** and **S2**. The calculation steps and relevant data are referred from Betz's work.¹⁰ At cell level, the energy density conversion rate of state-of-the-art classic LIBs from theoretical to practical value is only ~44 wt.%/~33 vol.%¹⁰, while they can be improved up to ~55 wt.%/~41 vol.% in *b*-LIBs (100 units). When it comes to system level, the difference will be expanded further (~30 wt.% for classic LIBs and ~50 wt.% for *b*-LIBs) due to the additional components of power supply system for classic LIBs. The energy density at system level can be improved 67% from classic LIBs to *b*-LIBs cell configuration. Therefore, how to realize such ideal *b*-LIBs worth more efforts.

Ideal *b*-LIBs demand anodes with intermediate cutoff voltage (≥ 0.5 V) to prevent lithiation of Al foil (~0.3 V), thus exclude the commercial graphite and Si/C anodes, let alone the Li metal anodes. Metal oxide anodes with relatively high charge/discharge voltage are considered difficult to obtain an energy density higher than that of classic LIBs with graphite anode^{11, 12}. However, such a property is intrinsically suit for the *b*-LIBs. As shown in **Figure 1D**, the estimated anode capacity (cutoff voltage ≥ 0.5 V), average charge potential, and estimated energy density of full cells for these metal oxide materials and relevant materials are summarized. Our newly developed La doped LiCoO_2 ¹³ with high cutoff voltage of 4.6 V and high specific capacity of 210 mA h g⁻¹ is assumed as the cathode. The speculated energy density of full cells with intercalation-type oxide

anodes (*e.g.* $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Nb_2O_5 , and TiO_2) mainly ranges from 200 to 300 Wh kg^{-1} , which can be enhanced to 300~350 Wh kg^{-1} by applying conversion-type oxide anodes (*e.g.* Mn_3O_4 , MoO_2 , NiO , and Co_3O_4). Iron oxide anodes, which have proper voltage and deliver most of the capacity under the voltage range of 0.5 – 3.0 V, can even make the energy density of full cell exceed 400 Wh kg^{-1} , as exhibited in **Figure 1D**. Yet the critical issues of iron oxide anode on capacity fading and inefficient rate capability are still need to be overcome.

Herein, a rational designed amorphous Li^+ conductive Li-Fe- BO_2 (LFBO) matrix is introduced to the iron oxides ($\text{Fe}_3\text{O}_4 + \text{Fe}_2\text{O}_3$ mixed phase) anode (FeO_x -LFBO), which was successfully prepared by an newly developed electrostatic adsorption coprecipitation method. Such a LFBO matrix can serve as a Li^+ conductor/reservoir to enable fast Li^+ diffusion, a heterogeneous nano-reactor to interdict aggregation of Fe + Li_2O precipitates, a binder to ameliorate contact between particles, and a soft buffer to remit volume change. The FeO_x -LFBO has a high tap density of 1.6 g cm^{-3} (much superior to graphite, Si/C, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, ~0.8 – 1.2 g cm^{-3}), good electronic conductivity, and unexpected high Li^+ conductivity. Under the voltage range of 0.01 – 3.0 V, FeO_x -LFBO harvests the admirable capacity of 933 mA h g^{-1} at 0.5 A g^{-1} , excellent cycling stability (capacity retention 99% after 1000 cycles at 5 A g^{-1}), and capacitive rate capability (683 mA h g^{-1} at 20 A g^{-1} and 384 mA h g^{-1} at 50 A g^{-1}). With the intermediate cutoff voltage of 0.5 V, FeO_x -LFBO anode still maintains 709, 436, and 192 mA h g^{-1} at 0.5, 20, and 50 A g^{-1} , respectively, much better than state-

of-the-art anodes. For the first time, a novel Cu-free LIB is assembled by our newly developed La-LCO cathode and FeO_x-LFBO anode, delivering a competitive energy density of ~350 Wh kg⁻¹ and outstanding power density of ~6700 W kg⁻¹. Moreover, a prototype Cu-free solid-state bipolar pouch full cell is also fabricated successfully with high voltage of 7.6 V and great cycling stability.

Results

Experimental demonstration. FeO_x-LFBO was successfully prepared by a facile synthetic method, as schematic illustrated in **Figure 2A**. Fe(OH)₃ · Fe³⁺ colloidal particles were obtained by a facile boiling water method, which can absorb BO₂⁻ through electrostatic interaction and some Li⁺ (from LiBO₂) to form a Li-Fe-BO₂ coated Fe(OH)₃ co-precipitates. After aging 12 hours, these precipitates were separated, dried, and then annealed in Ar flow at 500 °C to obtain FeO_x-LFBO. Referenced sample FeO_x was obtained by the same processing without adding LiBO₂. The morphology of FeO_x with Li⁺ conductive LFBO matrix was confirmed by transition electron microscopy (TEM), as shown in **Figure 2B**. FeO_x-LFBO sample shows the big secondary particle, which is composed of Fe₂O₃, Fe₃O₄ (confirmed by **Figure S3A**), and the amorphous matrix. More clearly amorphous LFBO layer can be observed at the surface of FeO_x particles by high resolution TEM (HRTEM) with the thickness of 3.7 – 4.5 nm, as shown in **Figure 2C-D**. The phase of these particles can be confirmed by measuring the interplanar spacing (0.365 nm for Fe₂O₃ (012) and 0.267 nm for Fe₂O₃ (104)), angle between the crystal faces (47° for Fe₂O₃ (012)/(104) and 27°

for Fe_2O_3 (012)/(116)) and corresponding fast fourier transform (FFT) patterns, as shown in **Figure 2D-E**. For comparison, bare FeO_x sample is consisted of loosely packed particles with the size of 50-200 nm, and the the suface is clean (**Figure S3B-C**).

Figure 2. Schematic synthetic processing and basic characterization of $\text{FeO}_x\text{-LFBO}$. (A) Schematic synthetic processing of $\text{FeO}_x\text{-LFBO}$. (B) TEM images of $\text{FeO}_x\text{-LFBO}$ sample. Inset: Corresponding SAED patterns (Fe_2O_3 and Fe_3O_4). (C-D) HRTEM images of $\text{FeO}_x\text{-LFBO}$ sample with amorphous Li-Fe- BO_2 coating layer. (E) Corresponding FFT patterns of (D). (F) XRD patterns, (G) N_2 adsorption-desorption isotherms, and (H) electronic conductivity of the pressed pellets of $\text{FeO}_x\text{-LFBO}$ and FeO_x samples. (I) Enlarged Nyquist plots spanning over 0.01– 10^5 Hz of $\text{FeO}_x\text{-LFBO}$ ceramic tablet. Inset: Randles equivalent circuit.

To further identify the components, X-ray diffraction (XRD) was utilized. The unannealed sample shows highly amorphous XRD patterns (**Figure S4A**) while annealed products contained two phase, Fe_2O_3 (JCPDS No. 33-0664) and Fe_3O_4 (JCPDS No. 19-0629), as shown in **Figure 2F**. To be noted, no signal of B

species is observed in XRD patterns, indicating B species may be amorphous. Since Li and B are light elements, which cannot be detected by energy dispersive spectroscopy (EDS), thus we use inductively coupled plasma-atomic emission spectrometry (ICP-AES) to determinate the element ratio of Li : B : Fe, which is $\sim 1:2:5.2$, indicating the composition of $\text{FeO}_x\text{-LFBO}$ is $\text{FeO}_x \cdot \text{Li}_{0.2}\text{Fe}_{0.1}\text{B}_{0.4}\text{O}_{0.8}$. As shown in **Figure S4B**, and **2G**, the specific surface area (SSA) of $\text{Fe}(\text{OH})_3$ precipitates and $\text{Fe}(\text{OH})_3\text{-LFBO}$ precipitates are $289.56 \text{ m}^2 \text{ g}^{-1}$ and $297.21 \text{ m}^2 \text{ g}^{-1}$, respectively, which reduce to $15.36 \text{ m}^2 \text{ g}^{-1}$ and $8.42 \text{ m}^2 \text{ g}^{-1}$. Obviously, the SSA and the pore volume of FeO_x with LFBO matrix are much lower than the bare FeO_x , which may benefit the initial coulombic efficiency, durability, and rate capability. Besides, the tap density of $\text{FeO}_x\text{-LFBO}$ was also measured, which is as high as $\sim 1.6 \text{ g cm}^{-3}$, much higher than that of carbon-contained anode materials.

We expect that $\text{FeO}_x\text{-LFBO}$ may have better electronic conductivity than bare FeO_x due to the adhesive effect of amorphous LFBO induced lower crystal interface resistance. To confirm, $I\text{-}V$ curves of pressed pellets ($\sim 0.5 \text{ g}$ samples, $\Phi = 13 \text{ mm}$, thickness $\sim 1 \text{ mm}$) of FeO_x and $\text{FeO}_x\text{-LFBO}$ were measured at room temperature. In **Figure 2H**, the apparent conductivity of $\text{FeO}_x\text{-LFBO}$ is higher than that of FeO_x by about 4.3 times, demonstrating that the interface resistance is the dominate issues. $\text{FeO}_x\text{-LFBO}$ was sintered to a ceramic tablet ($\sim 2 \text{ mm} \times 4 \text{ mm}$ with the thickness of $\sim 0.7 \text{ mm}$) by spark plasma sintering (SPS) at 500°C with Ar protection. This tablet was then coated by silver paste on both side, dried,

and clamped by stainless steel sheet. As shown in **Figure 2I**, the EIS test of such a tablet was performed spanning over 0.01 Hz to 10^5 Hz (5 mV excitation), also see the Randles equivalent circuit. The Nyquist plot shows a typical properties of solid-state electrolyte, with a half circle at high frequency and a tail at middle-to-low frequency. The slope of the tail is quite low because of low ion diffusion efficiency of the sample. The calculation of ionic conductivity is based on $\sigma = d/(RS) = 1.4 \text{ mS cm}^{-1}$, where d is the thickness ($\sim 0.7 \text{ mm}$), S is the area ($\sim 2 \text{ mm} \times 4 \text{ mm}$), R is total resistance ($612 \text{ } \Omega$, fitted by Zview 2). On the contrary, the bare FeO_x sample shows meaningless splashes because it is not an electrolyte for ions. We suspect the origin of this unexpected ionic conductivity is originated from the amorphous Li-Fe- BO_2 matrix, and the FeO_x may work as the fillers with enhanced effect¹⁴. Therefore, the amorphous LFBO matrix may work as a Li^+ diffusion “expressway”, a space-confined “nano-reactor”, and a Li^+ “reservoir” to enable fast response of electrochemical reaction.

Electrochemical performance of FeO_x -LFBO anode. Benefiting from this unique matrix, FeO_x -LFBO electrode (counter electrode being a lithium foil) achieves excellent electrochemical performances. As shown in **Figure S5**, although achieving a high capacity at the beginning, unmodified FeO_x anode exhibits the poor cycling durability, whose capacity fades to 100 mA h g^{-1} within only 50 cycles at galvanostatic charge-discharge (GCD) test of 0.1 A g^{-1} . On the contrary, FeO_x -LFBO anode delivers a little lower specific capacity of $\sim 870 \text{ mA h g}^{-1}$ ($\sim 1400 \text{ mA h cm}^{-3}$) but harvests high initial coulombic efficiency of $\sim 75\sim 80\%$

and great durability at 0.1 A g^{-1} , which may be due to the extra component of “electrochemical inert” Li-Fe-BO₂ matrix. The capacity of FeO_x-LFBO increases during the following cycles with the top capacity over 1700 mA h g^{-1} ($2720 \text{ mA h cm}^{-3}$, the mechanism of capacity increasing will be discussed later).

Figure 3. Electrochemical performance of FeO_x-LFBO anode. (A) Nyquist plots spanning over 0.01–10⁵ Hz of FeO_x-LFBO and FeO_x electrodes. Inset: Randles equivalent circuit and enlarged Nyquist plots. (B) Rate capability of FeO_x-LFBO and FeO_x electrodes. (C) Long-term cycling of FeO_x-LFBO at 5 A g⁻¹. Inset: Illustrated electrochemical reaction mechanism of FeO_x-LFBO anodes. Comparison of the (D) specific gravimetric and (E) volumetric rate capability among the reported and commercial anode materials. (F) GITT profiles of FeO_x-LFBO and FeO_x electrodes and (G) the relevant Li⁺ diffusion coefficient with different delithiation during charging or discharging. (H) The capacitance ratio fitting at 0.7 mV s⁻¹.

Initial five cyclic voltammetry (CV) curves of FeO_x-LFBO and FeO_x electrodes (**Figure S5**) were obtained at the scan rate of 0.3 mV s⁻¹ over a voltage window of 3.0 – 0.01 V. Specifically, for FeO_x-LFBO (**Figure S6A**), the first-cycle reduction peak at ~1.3 V is belonged to the formation of Li_nFeO_x¹⁵, which shifts to ~1.4 V afterwards due to the electrode activation and remains stable. This peak is very weak in FeO_x (**Figure S6B**), which may because of its lower electronic and ionic conductivity. A strong and broad peak located at ~0.6 V present the conversion reaction of FeO_x (or Li_nFeO_x) and the formation of surface electrolyte interface (SEI) layer, which shift to ~0.7 V after initial cycle. The peak near 0 V may result from the Li storage of B species, as indicated by our previous work¹⁶. The bare FeO_x have the similar but sharper peak located at ~0.6 V in the first-cycle, which shift to ~0.9 V later. This difference may be due to the pre-lithiation reaction of FeO_x-LFBO at ~1.4 V (Li_nFeO_x), while FeO_x does not. The broad oxidation peak located at ~1.8 V is the oxidation reaction. The shape of CV curves are also related to the dynamic properties of the electrode, and the “fatter” curves of FeO_x-LFBO imply the fast lithium storage.

Further electrochemical performance was investigated by EIS of FeO_x-LFBO/Li half cell (0.01 Hz to 10⁵ Hz, 5 mV excitation). As shown in **Figure 3A**, the equivalent series resistance (R_e) and charge transfer resistance (R_{ct}) of FeO_x-LFBO electrode is 2.8 Ω and 40 Ω, respectively, much small than those (11 Ω and 202 Ω) of the FeO_x electrode (fitted by Zview2). Smaller R_e and R_{ct} of FeO_x-LFBO indicate the better electronic conductivity, which is consistent with result

in **Figure 2H**. Furthermore, the slope of the tail at middle-low frequency present the Warburg resistance (Z_w). Obviously, the slope of FeO_x-LFBO electrode is bigger, indicating the faster Li⁺ diffusion (capacitive-like Li⁺ diffusion) than FeO_x electrode. The above in-direct evidences imply that FeO_x-LFBO may serve better performance in fast charge/discharge.

Direct rate capability test spanning over 0.2 A g⁻¹ to 50 A g⁻¹ was also performed with the active material loading mass of ~1.0 mg cm⁻², as shown in **Figure 3B**. The specific capacities are ~906, 936, 911, 896, 848, 791, 680, and 380 mA h g⁻¹ (~1450, 1498, 1458, 1434, 1357, 1266, 1088, and 608 mA h cm⁻³) at 0.2, 0.5, 1, 2, 5, 10, 20, and 50 A g⁻¹, respectively. From initial current density of 0.2 to 20 A g⁻¹, the capacity retention is up to 75 %, much superior to the most reported results¹⁵⁻³⁶, as shown in **Figure 3C-D**. Long-term cycling of FeO_x-LFBO at 1, 2, and 5 A g⁻¹ were also performed after initial 10 cycles at 0.1 A g⁻¹. The initial capacities of all three cells are ~870 mA h g⁻¹, while the capacities increase gradually at 1 and 2 A g⁻¹ until up to ~1500 mA h g⁻¹ after 400 – 500 cycles (**Figure S7**), similar with it is at 0.1 A g⁻¹ (**Figure S5**). At a large current density of 5 A g⁻¹, the capacity maintain stable with the retention of 98.9% even after 1000 cycles, reaching the demands of commercial application, as shown in **Figure 3E**. Besides, similar strategy of introducing Li⁺ conductive matrix was also applied in developing MnO_x, CoO_x, and SnO₂ based anode materials, whose electrochemical performance are also improved significantly, as shown in **Figure**

S8. Other lithium salts such as Li_2SO_4 , Li_2CO_3 , and LiCl , were also confirmed to show the similar performance improvement effect, as we reported before.³⁷

In order to apply Al foil, the rate and cycling performance of $\text{FeO}_x\text{-LFBO}$ with the intermediate cutoff voltage of 0.5 V were also evaluated, as shown in **Figure S9**. The specific capacity $\text{FeO}_x\text{-LFBO}$ at 0.5 C is $\sim 710 \text{ mA h g}^{-1}$ under the voltage range of 3.0 – 0.5 V (safe cutoff voltage for Al foil), $\sim 76\%$ of that in 3.0 – 0.01 V. Even at the high rate of 20 and 50 A g^{-1} , it can also reach up to ~ 440 and $\sim 200 \text{ mA h g}^{-1}$ (**Figure S10A**). The cycling stability of $\text{FeO}_x\text{-LFBO}$ under the voltage range of 3.0 – 0.5 V is also excellent, maintaining over 95% capacity after 1000 cycles at 5 A g^{-1} , as shown in **Figure S10B**.

Mechanism Analysis. Such an extremely stable cycling performance is originated from the novel structure of $\text{FeO}_x\text{-LFBO}$, in which LFBO glass is a relatively soft and has better Li^+ conductivity than Li_2O ³⁸⁻⁴⁵. Therefore, this LFBO matrix can serve as a Li^+ conductor/reservoir to enable fast response and diffusion of Li^+ , a heterogeneous nano-reactor to interdict aggregation of Fe + Li_2O precipitates, a binder to ameliorate contact between particles, and a soft buffer to remit volume change, as illustrated in the inset of **Figure 3E**. Specifically, FeO_x little particles can gather to become big secondary particle with LFBO glass matrix, as illustrated in **Figure 2A** and confirmed by TEM image (**Figure 2B-D**). This LFBO glass matrix can reduce the interface electronic resistance and supply Li^+ at the first beginning of electrochemical lithiation reaction (Li^+ conductor/reservoir, **Figure S11A-B**). Thereafter, Li^+ in

the electrolyte may replenish into LFBO matrix to balance the electric charge (**Figure S11B-2**). Thanks to such fine interface phase contact of FeO_x and Li^+ source, the conversion reaction of FeO_x occurs more uniform (**Figure S11C**) and complete (**Figure S11D**) even at high rate. Moreover, as a heterogeneous layer, LFBO can interdict the movement and diffusion of Li_2O and involved Fe from initial particles (**Figure S11D-1, 2**), thus prevent the agglomerates of small particles to a bigger one. And as a soft buffer, it can also act like the elastic ‘plasticine’ to remit the volume expansion and electrode cracking. For comparsion, without LFBO matrix, bare FeO_x electrode may suffer a fast particle coarsening and cracking (**Figure S12**), exhibiting quick capacity fading and bad rate capability (**Figure 3B** and **S5**). As shown in **Figure S13**, FeO_x nanoparticles are embedded in the LFBO materix without aggregation in cycled FeO_x -LFBO electrode (500 cycles at 2 A g^{-1}) while the particles are coarsed seriously in FeO_x electrode.

To reveal the origin of the superior rate capability of FeO_x -LFBO, galvanostatic intermittent titration technique (GITT) was employed to study the electrode thermodynamics and kinetics process of FeO_x -LFBO and FeO_x electrodes and the diffusion coefficients were calculated under various potentials, as shown in **Figure 3F-G**. The Li^+ diffusion coefficients were quantified according to the equation below.

$$D = \frac{4}{\pi\tau} \left(\frac{mV_m}{MS} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (1)$$

where τ is the relaxation time (2400 s), m is the mass of iron oxides (based on Fe_2O_3), V_m is the molar volume, M is the molar mass, and S is the surface area of the electrode. ΔE_s and ΔE_τ are obtained from **Figure 3E**. Apparently, the diffusion coefficients of $\text{FeO}_x\text{-LFBO}$ are much higher than that of FeO_x during both the lithiation and delithiation reactions. the average the diffusion coefficient D_{Li} of $\text{FeO}_x\text{-LFBO}$ is $\sim 6.4 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, much superior to FeO_x and other metal oxide anodes.^{37, 46}

Further dynamic analysis was carried out by testing the CV curves at different scan rate over $0.3 - 0.7 \text{ mV s}^{-1}$. As shown in **Figure S14A-B**, $\text{FeO}_x\text{-LFBO}$ and FeO_x electrodes exhibit different properties, where the reduction current peaks are located at 0.735 V and 0.696 V at 0.3 and 0.7 mV s^{-1} , respectively. Thus the difference value is only 39 mV, much smaller than 84 mV of the FeO_x electrode, which means $\text{FeO}_x\text{-LFBO}$ electrode has weaker voltage/ohmic polarization effect, leading to the better kinetic characteristics in electrode interface and lithium ion diffusion⁴⁷. It also indicates that the LFBO matrix can weaken the space potential layer, lower the surface potential, and restrain the side reaction to enhance the durability of the electrode. This result support the extraordinary rate capability (**Figure 3B**) and excellent long-term cycling performance (**Figure 3E**), and also consistent with the previous work⁴⁷. Furthermore, according the relationship between the current and the scan rate^{48, 49}:

$$I = av^b \quad (2)$$

where I is the current, v is the scan rate. Here we choose oxidation current peak at ~1.8 V of FeO_x-LFBO electrode because it is a single peak. As shown in **Figure S14C**, $-\log(i)$ vs. $-\log(v)$ plot appears to be a liner relationship with the slope of (b -value) of 0.88. As suggested by Dunn *et al.*⁴⁹, a b -value of 0.5 would indicate that the current is controlled by semi-infinite linear diffusion (battery), a value of 1 indicates that the current is surface-controlled (supercapacitor). Therefore, FeO_x-LFBO electrode has a capacitive-like electrochemical Li storage property, which is further confirmed by capacitance ratio fitting by followed equation in **Figure 3H**:

$$I = k_1v + k_2v^{1/2} \text{ or } I/v = k_1 + k_2 v^{-1/2} \quad (3)$$

As a result, the capacitance ratio in FeO_x-LFBO electrode can reach up to 85.5%. This unexpected high value is resulted from the uniform interface lithiation/delithiation mechanism, which is induced by the Li⁺ conductive LFBO matrix.

Aside from the dynamic properties, another interesting phenomenon of FeO_x-LFBO electrode is the capacity increasing along with the cycling when the current density < 5 A g⁻¹. To identify the origin of this increased capacity, GCD curves at 2 A g⁻¹ are analyzed. As shown in **Figure S15A**, the discharge capacity can be divided to two parts base on the voltage range of 3 – 0.7 V and 0.7 – 0.01 V. The capacity in 3 – 0.7 V is contributed by conversion reaction of FeO_x, which is ~650 mA h g⁻¹ and remains stable along with the cycling. The capacity in 0.7 V – 0.01 V can be attributed the lithium storage of B species, as indicated in our

previous work¹⁶. This reaction is difficult to occur at first but may be activated during the long-term cycling and thus contribute increasing capacity. The relevant capacity contribution vs. cycle number in different voltage ranges of 3.0 – 0.7 V and 0.7 – 0.01 V is shown in **Figure S15B**. Obviously, the capacity ratio in 3.0 – 0.7 V decrease from the initial 74.6 % to 41.7 % after 500 cycles, while the capacity ratio in 0.7 – 0.01 V increase from the initial 25.4 % to 58.3 %, demonstrating the gradual enhanced lithium storage properties of B species.

In order to confirm the above suspect, we performed the *ex-situ* B 1s X-ray photoelectron spectroscopy (XPS) of cycled FeO_x-LFBO electrodes. Normally, trivalent B 1s is located at ~192 eV, and it is deemed incapable of storing Li¹⁶. However, as shown in **Figure S15C**, after initial discharge to 0.01 V, a weak peak located at 189 eV can be also identified, which presents the extra-lithiated B. However, the ratio of this part is small, meaning that the most of B is inert and cannot storage Li, thus supply less capacity. After 500 cycles and discharge to 0.01 V, the peak located at 189 eV becomes major peak, consistent with the capacity increasing in **Figure S15A**. And after 500 cycles and charge to 3.0 V, the B 1s peak returns to higher binding energy, indicating the Li storage of B specie is highly reversible. It can be found that the capacity increasement become slower along with the improvement of the current density. It is because the Li⁺ storage of B species is dynamically difficult thus cannot be activated at high rates.

Figure 4. Fabrication and electrochemical performance of Cu-free LIBs and *b*-LIBs full cells with $\text{FeO}_x\text{-LFBO}$ anodes. (A) Schematic image of Cu-free $\text{Al}|\text{La-LCO}||\text{FeO}_x\text{-LFBO}|\text{Al}$ full cell. (B) Illustrated GCD curves of our newly developed La-LCO and $\text{FeO}_x\text{-LFBO}$. (C) GCD curves of $\text{Al}|\text{La-LCO}||\text{FeO}_x\text{-LFBO}|\text{Al}$ and $\text{Al}|\text{LCO}||\text{FeO}_x\text{-LFBO}|\text{Cu}$ full cells at 1 C. (D) Rate capabilities of $\text{Al}|\text{La-LCO}||\text{FeO}_x\text{-LFBO}|\text{Al}$, $\text{Al}|\text{LCO}||\text{FeO}_x\text{-LFBO}|\text{Cu}$, and traditional $\text{Al}|\text{LCO}||\text{C}|\text{Cu}$ full cells ranging from 1 – 20 C. (E) Long-term cycling of $\text{Al}|\text{La-LCO}||\text{FeO}_x\text{-LFBO}|\text{Al}$ full cell at 2 C. (F) Schematic image of Cu-free solid-state *b*-LIB. (G) The digital image of pouch-type bipolar solid-state cell and a flexible LED light showing “SICCAS”. (H) GCD curves Cu-free $\text{Al}|\text{La-LCO}||\text{FeO}_x\text{-LFBO}|\text{Al}|\text{La-LCO}||\text{FeO}_x\text{-LFBO}|\text{Al}$ bipolar solid-state cell. (I) Long-term cycling and relevant GCD curves of $\text{Al}|\text{La-LCO}||\text{FeO}_x\text{-LFBO}|\text{Al}|\text{La-LCO}||\text{FeO}_x\text{-LFBO}|\text{Al}$ bipolar solid-state cell.

Electrochemical performance of Cu-free LIBs. To evaluate the potential of FeO_x-LFBO anode in practical application, electrodes with different loading mass spanning over 1.5 – 6.0 mg cm⁻² are tested. As shown in **Figure S16**, capacities of various electrodes at low current density are similar, while the high rate capabilities exhibit great difference. Electrodes with the loading mass of 1.5 and 2.3 mg cm⁻² show similar performance until the current density increase to 5 A g⁻¹ (capacity of ~680 mA h g⁻¹), and remaining impressive capacities of ~460 and 320 mA h g⁻¹ even at 20 A g⁻¹, respectively. Electrode with the loading mass of 3.0 mg cm⁻² also shows high capacity retention of ~580 mA h g⁻¹ at 5 A g⁻¹ but reduces to only ~220 mA h g⁻¹ at 10 A g⁻¹. Higher loading mass could make the high rate capacity lower.

We applied our newly developed La-doped LiCoO₂ cathode¹³ (cutoff voltage 4.6 V, ~210 mA h g⁻¹) and FeO_x-LFBO anode (3.0 – 0.5 V, 710 mA h g⁻¹) to fabricate Cu-free sandwich structured full cells, as shown in **Figure 4A-B**. For comparison, cells with commercial LiCoO₂ (cutoff voltage 4.2 V, ~140 mA h g⁻¹) cathode and FeO_x-LFBO anode (3.0 – 0.01 V, ~930 mA h g⁻¹) were also assembled (**Figure S17** and **4C**). The loading masses of cathode materials are both ~10 mg cm⁻², while the matching loading masses of FeO_x-LFBO anodes are ~3.0 and 1.6 mg cm⁻², respectively (N:P ratio = 1.01~1.05). The assembled full cells were both estimated under the voltage range of 4.1 – 1.0 V. The GCD curves of Al|La-LCO||FeO_x-LFBO|Al and Al|LCO||FeO_x-LFBO|Cu full cells are shown in **Figure 4C**, indicating that specific capacity of two cells are ~160 and ~120

mA h g⁻¹ (basing on the total mass of cathode and anode active materials), respectively. The average discharge voltages of two cells are both ~2.2 V. The rate capabilities of Al|La-LCO||FeO_x-LFBO|Al and Al|LCO||FeO_x-LFBO|Cu full cells were evaluated, as shown in **Figure 4D**, which can harvest ~60 and ~40 mA h g⁻¹ even at a ultrahigh rate of 20 C, much better than traditional Al|LCO||C|Cu cell. Therefore, Al|La-LCO||FeO_x-LFBO|Al can deliver a competitive energy density of ~ 350 Wh kg⁻¹ at 1 C (theoretical energy density of ~230 Wh kg⁻¹ if using Li₄Ti₅O₁₂ anode) and an outstanding power density reaching up to ~6700 W kg⁻¹ at 20 C. Besides, the cycling stability of Al|La-LCO||FeO_x-LFBO|Al was also performed at 80%DOD, which can remain ~75% after long-term cycling of 2000 cycles, as shown in **Figure 4E**.

Electrochemical performance of Cu-free solid-state b-LIBs. To evaluate the feasibility of FeO_x-LFBO anode to apply to *b*-LIBs, a prototype Cu-free Al|La-LCO||FeO_x-LFBO|Al|La-LCO||FeO_x-LFBO|Al bipolar solid-state pouch-type cell was fabricated, as shown in **Figure 4F**. Bipolar electrode is prepared by coating La-LCO cathode and FeO_x-LFBO anode slurries on both sides of the same Al foil separately. High performance solid-state PVDF/LLZO/LiTFSI electrolyte⁵⁰ are applied with trace liquid electrolyte (~2 wt.%) to wet the electrode-electrolyte interface. The electrodes and solid-state films were stacked layer by layer and then rolled to enhance the interface contact, and finally cut to desired shape. The encapsulated pouch cell is exhibited in **Figure 4G**, which illuminates a flexible LED light. The relevant GCD curves (**Figure 4H**) indicate

that such a Cu-free Al|La-LCO||FeO_x-LFBO|Al|La-LCO||FeO_x-LFBO|Al bipolar solid-state cell can deliver a high voltage of 7.6 V with the specific capacity of ~70 mA h g⁻¹ (based on the total active materials). Therefore, the energy density of such a *b*-LIBs can reach up to ~310 Wh kg⁻¹, which is roughly equivalent to Cu-free LIBs. Moreover, the cycling stability of such a high voltage *b*-LIB is excellent, whose capacity retention can reach up to 92% after 100 cycles at 0.15 C, as shown in **Figure 4I**. Besides, to evaluate the safety of such a Cu-free solid-state *b*-LIBs, pouch cells under bended, heated, and cut conditions were performed, which can still light the red LED bulbs without smoke and fire, as shown in **Figure S18**.

Conclusions

In summary, in order to satisfy the critical demands of *b*-LIBs, a rational designed amorphous Li⁺ conductive LFBO matrix confined FeO_x anode was successfully prepared by a facile developed electrostatic adsorption coprecipitation method. This LFBO matrix can serve as a Li⁺ conductor/reservoir to enable fast Li⁺ diffusion, a heterogeneous nano-reactor to interdict aggregation of Fe + Li₂O precipitates, a binder to ameliorate contact between particles, and a soft buffer to remit volume change. This FeO_x-LFBO have a high tap density, good electronic conductivity, and high Li⁺ conductivity. As the anode of LIB, it harvests the admirable capacity, excellent cycling stability, and capacitive rate capability. Cu-free classic sandwich structured full cell with FeO_x-LFBO anode is fabricated, delivering a competitive energy density of ~ 350 Wh kg⁻¹ at 1 C and an outstanding power density reaching up to ~6700 W kg⁻¹ at 20 C.

Moreover, a prototype bipolar solid-state cell is also assembled, which can achieve a high voltage of 7.6 V and good cycling stability. This study may set off an upsurge in the research of intermediate cut-off voltage anodes for the novel solid-state *b*-LIBs, such as oxides, sulfides, nitrides, and phosphorus based anodes.

Methods

All chemicals used in this work were analytical pure without any further purification and commercially available. Deionized water used was house generated. (Resistivity: $0.860\text{ M}\Omega\cdot\text{cm}$ at $25\text{ }^{\circ}\text{C}$, which is tested by Rex DDSJ-308F Conductivity Meter).

Synthesis of FeO_x and $\text{FeO}_x\text{-LFBO}$: FeO_x were prepared by a simple hydrolysis precipitation method followed by an Ar atmosphere annealing processing. Briefly, 2.70 g $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (0.01 mol) was solved in 10 mL DI water, which was then added into 200 mL boiling DI water under stirring to obtain $\text{Fe}(\text{OH})_3\cdot\text{Fe}^{3+}$ colloidal solution. After aging 12 hours, these precipitates were separated, washed, freeze dried, and then annealed in Ar flow at $500\text{ }^{\circ}\text{C}$ for 4 hours. $\text{FeO}_x\text{-LFBO}$ was prepared by the electrostatic adsorption coprecipitation method. Specifically, LiBO_2 (2.50 g, 0.05 mol) solutions (45 mL) was added into the above $\text{Fe}(\text{OH})_3\cdot\text{Fe}^{3+}$ colloidal solution. The mixed solution was stirred for 12 hours before separation. The obtained product was freeze dried directly without washed, and the dried powder was annealed as above.

Synthesis of $\text{CoO}_x\text{-LBO}$, $\text{MnO}_x\text{-LBO}$, and $\text{SnO}_2\text{-LBO}$: $\text{CoO}_x\text{-LBO}$, $\text{MnO}_x\text{-LBO}$, and $\text{SnO}_2\text{-LBO}$ samples were obtained following a simple precipitation

process. Specifically, 0.01 mol of cobalt (II) chloride, manganese (II) chloride, and tin (IV) chloride was first dissolved in 100 mL of DI water, and then 50 mL of LiOH solution (0.6 mol L^{-1}) was added to the solution under stirring. LiBO_2 (2.50 g, 0.05 mol) solutions (45 mL) was added into the above solution. After stirring for 12 h, the precipitate was separated, freeze dried, and then annealed in Ar flow at 500°C for 4 hours. LiOH was used as the precipitant since these metal ions cannot form colloidal particles by boiling water method.

Material characterization. Nitrogen adsorption-desorption isotherms at 77 K were measured by an Accelerated Surface Area & Porosimetry system (ASAP2020, Micrometer) using vacuum-degassed samples (120°C for at least 4 h). These isotherms were used to calculate the specific surface area by the Brunauer-Emmett-Teller (BET) method. The chemical composition of the hybrid material was confirmed thru Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Prodigy 7 of Leeman Ltd.) to measure the atomic ratio of Li, Fe, and B. The microstructures were characterized by transmission electron microscopy (TEM, JEM2010-HR). Powder X-ray diffraction (XRD) patterns were collected using a Bruker D2 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($k = 1.5418 \text{ \AA}$) at a scanning rate of 2° min^{-1} in the 2θ range of $5^\circ - 80^\circ$. X-ray photoelectron spectroscopy (XPS, Axis Ultra of Kratos Analytical Ltd. $\text{Al K}\alpha$ radiation, $h\nu = 1486.7 \text{ eV}$) was calibrated using the 284.8 eV peak of delocalized sp^2 -hybridized carbon that appeared on every sample due to atmospheric contamination. This procedure was repeated at the beginning of every XPS data

analysis. Cycled samples were washed 3 times by dimethyl carbonate (DMC) to remove the residue electrolyte salts before XPS measurements.

Electrochemical measurements. An slurry consisting of 80 wt.% active material ($\text{FeO}_x\text{-LFBO}$ and FeO_x), 10 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride (PVDF/N-methyl pyrrolidinone) was uniformly coated to a Cu/Al foil. Electrodes with different loading mass were obtained by using different thickness coater. The coated foil was dried at 100 °C for 12 hours in oven, then cut into disk electrodes of 12 mm in diameter. After that, the electrodes were further vacuum-dried overnight at 60 °C. Lithium foil (China Energy Lithium Co., Ltd.) was used as the counter and reference electrode, and Celgard separator. The electrolyte used was 1 mol L⁻¹ LiPF₆ in a 1: 1: 1 volume mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC). Classic full coin cell was assembled by commercial LCO cathode, graphite anode, Celgard separator, and 1 mol L⁻¹ LiPF₆ electrolyte. The negative to positive capacity ratio (N/P ratio) is $\sim 1.10 \pm 0.01$. Cu-free full cell with sandwich structure is fabricated by using our newly developed La-LCO cathode¹³, $\text{FeO}_x\text{-LFBO}$ anode, and same separator/electrolyte. The N/P ratio is 1.05 ± 0.01 . Cu-free bipolar full cell with 2 units is fabricated by using our newly developed La-LCO cathode, PVDF/LLZO/LiTFSI solid-state electrolyte⁵⁰ with 2 wt.% liquid electrolyte, and $\text{FeO}_x\text{-LFBO}$ anode. The N/P ratio is 1.01 ± 0.01 . The loading masses of cathode for all full cells are $\sim 10 \text{ mg cm}^{-2}$. All cells were assembled in a recirculating argon glovebox, which reserved the moisture and

oxygen contents below 1 ppm. Electrochemical measurements were carried out on a LAND-CT2001C test system. The cycle lifetime of FeO_x-LFBO half cells were characterized at different rates within a voltage window of 3.0 – 0.01 V or 3.0 – 0.5 V. The rate capability was evaluated by varying the discharge–charge rate from 0.1 to 50 A g⁻¹. Full cells with sandwich structure were evaluated at 4.1 – 1 V. The rate capability was evaluated by varying the discharge–charge rate from 1 to 20 C. Pouch-type bipolar full cell was prepared and assembled in a dry room with a dew point below –41 °C. The assembled b-LIBs were first cycled for 2 cycles to complete the formation process before the long-term cycling at 7.6 – 2 V. Electrochemical impedance spectroscopy (EIS), room-temperature *I*-*V* characteristics, and cyclic voltammetry (CV) of the assembled coin cells were carried out using an automated electrochemical workstation (CHI660E and Autolab PGSTAT 302N from Switzerland). The EIS was measured between 0.01 Hz to 10⁵ Hz with an excitation voltage of 0.005 V at various potentials. The room-temperature *I*-*V* characteristics were accomplished in the voltage range of -0.3 V to +0.3 V at a scanning rate of 1 mV s⁻¹. The CV curves were obtained at a scanning rate of 0.3 mV s⁻¹ over the potential from 0.01 to 3.0 V vs. Li⁺/Li.

Theoretical energy density (*E*₀) of the full cell with FeO_x-LFBO anode is calculated by:

$$E_0 = \oint V dC = \oint V_{\text{cathode}} dC_{\text{cathode}} - \oint V_{\text{anode}} dC_{\text{anode}}$$

where *V* is voltage range of the full cell, *C* is the capacity based on the total active material mass of cathode and anode. Specifically, *V*_{cathode} is 3.0 – 4.6 V for La-

LCO with the loading mass of 10 mg cm^{-2} and the specific capacity of 210 mA h g^{-1} , and Vanode for $\text{FeO}_x\text{-LFBO}$ anode is $3.0 - 0.5 \text{ V}$ with the loading mass of 3.0 mg cm^{-2} and the capacity of 710 mA h g^{-1} . The practical energy density (E) of $\text{Al}|\text{La-LCO}||\text{FeO}_x\text{-LFBO}|\text{Al}$ is calculated by:

$$E = \oint V_{\text{cell}} dC$$

where V_{cell} is the voltage range $1 - 4.1 \text{ V}$ (average voltage is $\sim 2.2 \text{ V}$) of full cell with the capacity of 160 mA h g^{-1} . Therefore, the calculated practical energy density is $\sim 350 \text{ Wh kg}^{-1}$. And the power density $P = E/t$, which is $\sim 6700 \text{ W kg}^{-1}$ at 20 C .

Data availability

All data supporting the findings in the article as well as the Supplementary Information files are available from the corresponding authors on reasonable request.

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Author contributions

F.H. and W.D. proposed the idea of this work and wrote the manuscript. W.D. and Y. Z. designed and conducted the experiments. M.C. prepared the cathode materials. C. D. performed the TEM test. J. P. and W. M. prepared the solid-state electrolyte. Z. L. and H. D. performed some material characterizations. Y. T. fabricated and evaluated full cells. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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