Fibrous skeleton-framed, flexible high-energy-density quasi-solid-state lithium metal batteries

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Abstract
Despite the extensive investigation on solid-state lithium-metal batteries (SSLMBs), their application in flexible electronic devices has been plagued mainly by the physicochemical/mechanical instability of their electrode–electrolyte interfaces. Here, we present a fibrous skeleton-framed, quasi-solid-state LMB (fs-QSSLMB) as a new cell architecture concept to simultaneously achieve the high-energy-density, mechanical flexibility, and safety. The fs-QSSLMB is fabricated by embedding poly(ethylene terephthalate) (PET) nonwovens, stainless-steel meshes, and metal-coated conductive PET nonwovens with a lithiophilic-gradient morphology as customized fibrous skeletons into quasi-solid-state electrolytes (QSSEs), high-capacity LiNi0.8Co0.1Mn0.1O2 (NCM811) cathodes, and Li metal anodes, respectively. The stepwise printing of the NCM811 cathode/QSSE/Li anode assembly and the subsequent one-pot ultraviolet curing of the gel electrolyte precursors in the assembly enable the formation of seamless interfaces between the electrodes and QSSE, thereby ensuring the electrochemical sustainability and mechanical deformability of the fs-QSSLMB. In addition, owing to its fibrous skeleton-based structural uniqueness and seamless interfaces, the fs-QSSLMB exhibits electrochemical reliability, mechanical flexibility, safety (i.e., electrochemically active after being vertically cut in half and exposed to flame), and high (cell-based) gravimetric/volumetric energy densities (385 Wh kg−1cell/451 Wh L−1cell).

KEYWORDS
fibrous skeletons, flexibility, high-energy-density, lithium metal batteries, quasi-solid-state electrolytes, seamless interface

1 INTRODUCTION

With the emergence of the smart electronics and ubiquitous interconnectivity era, flexible/wearable devices, Internet of Things, and electric vehicles have attracted widespread attention, thus significantly increasing the demand for advanced power sources with high-energy-density, mechanical flexibility, and safety.1–3 Recently, solid-state lithium-metal batteries (SSLMBs) have garnered considerable attention as a promising energy storage system to fulfill the aforementioned requirements, owing to their high-energy-density, wide operating temperature range, and thermal stability.4–6
Li metals can provide a high theoretical capacity (3860 mAh g⁻¹), low density (0.534 g cm⁻³), and low electrochemical potential (~3.04 V vs. the standard hydrogen electrode), indicating their promising potential as an anode material for high-energy-density cells. However, the uncontrollable Li dendrite growth of Li metal anodes leads to short-circuit-induced safety failures, such as thermal runaway and explosion. To address this challenge, the use of solid-state electrolytes, such as inorganic, polymer, and organic/inorganic composite electrolytes, has been extensively explored. However, some factors have restricted the practical applications of SSLMBs, such as the poor interfacial contact between solid-state electrolytes and electrodes, insufficient electrochemical compatibility, grain boundary resistances, and fabrication complexity. Particularly, the significant increase in the interfacial resistance of Li metal anode when it is subjected to mechanical deformation has hindered the development of flexible SSLMBs. In addition to the solid-state electrolytes-related challenges, the poor mechanical flexibility of Li metal anodes and typical cathodes (composed of cathode active materials, conductive additives, and polymer binders on Al foil current collectors) has restricted the further application of SSLMBs.

In addition to the aforementioned flexibility issue, it is essential to consider a cell design that enables a high areal capacity and a low negative/positive electrode capacity (N/P) ratio to develop flexible high-energy-density SSLMBs. However, only few studies on SSLMBs have developed SSLMBs that could simultaneously achieve the high-energy-density, mechanical flexibility, and safety.

Here, to achieve this challenging goal, a new cell architecture concept, a fibrous skeleton-framed, flexible high-energy-density quasi-solid-state LMB (fs-QSSLMB), is presented. To achieve this design, poly(ethylene terephthalate) (PET) nonwovens, a Cu/Ni-deposited conductive PET nonwoven with lithiophilic Ag thin layers preferentially deposited at its bottom side, and a stainless-steel (SUS) mesh are embedded as customized fibrous skeletons into a quasi-solid-state electrolyte (QSSE), Li metal anode, and LiNi₀.₈Co₀.₁Mn₀.₁O₂ (NCM811) cathode, respectively, thereby ensuring the mechanical flexibility and structural integrity of the resulting fs-QSSLMB.

The QSSE is fabricated by incorporating a QSSE paste (consisting of a gel electrolyte precursor and alumina (Al₂O₃) nanoparticles) into a PET nonwoven using a solvent-drying-free printing process, after which the paste was subjected to ultraviolet (UV) curing. The NCM811 cathode is fabricated by printing a slurry mixture (consisting of NCM811 particles, carbon additives, and a gel electrolyte precursor) on a SUS mesh, after which the mixture is subjected to UV curing. In addition, the bottom side of the Cu/Ni-deposited PET nonwoven is coated with lithiophilic Ag thin layers using a sputter deposition method to prepare a three-dimensional (3D) flexible Li host with a lithiophilic-gradient morphology. Subsequently, Li was impregnated into the 3D Li host using electrochemical plating to produce a Li metal anode sheet.

The stepwise printing of the NCM811 cathode/QSSE/Li anode assembly and the subsequent one-pot UV curing of the gel electrolyte precursors in the assembly enable the formation of seamless interfaces between the electrodes and QSSE, which plays a viable role in ensuring the electrochemical sustainability and mechanical deformability of the resulting fs-QSSLMB.

Owing to its chemical and structural uniqueness (particularly, the customized fibrous skeletons and seamless interfaces), the resulting fs-QSSLMB exhibits electrochemical reliability, mechanical flexibility, safety (nonflammability), and high gravimetric/volumetric energy densities (385 Wh kg⁻¹/451 Wh L⁻¹), which are significantly higher than those of previously reported flexible solid-state LMBs.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Li foils and NCM811 (LiNi₀.₈Mn₀.₁Co₀.₁O₂) active materials were obtained from Honjo Chemical Co. and LG Energy Solutions, respectively. A PET nonwoven (thickness ~14 μm and porosity ~68%), Ni/Cu-plated conductive PET nonwoven (thickness ~35 μm and porosity ~72%), and SUS mesh (thickness ~60 μm and porosity ~50%) were obtained from Mitsubishi Paper Mills, Ajin ELECTRON, and Hebei Reking Wire Mesh Co. (China), respectively. PC and FEC were purchased from Sigma–Aldrich. LiFSI salts were provided by LG Energy Solutions (Korea). An electrolyte of 4 M LiFSI in PC/FEC = 93/7 (vol/vol) was prepared by mixing a solvent mixture (PC/FEC) with LiFSI in an argon-filled glove box.

2.2 | Fabrication of the printed QSSE membranes, fs-cathodes, and cPET/Ag-Li anodes

The QSSE paste was composed of a nonflammable gel electrolyte precursor (4 M LiFSI in (PC–FEC)/ETPTA = 90/10 (wt/wt), 1 wt% 2-hydroxy-2-methylpropiophenone was added as a photoinitiator) and Al₂O₃ nanoparticles (average powder size ~300 nm) at a composition ratio of 50/50.
The QSSE paste was printed on a PET nonwoven, after which the paste was subjected to a UV curing reaction using a Hg UV-lamp (Lichtzen) to obtain the self-standing and flexible fs-QSSLMBs. The cathode paste consisted of NCM811 powders, conductive additives (carbon black), and gel electrolyte precursor, in which the composition ratio of NCM811/carbon black/gel electrolyte precursor was 70/5/25 (wt/wt/wt). The cathode paste was printed on a SUS mesh, after which the paste was subjected to a UV curing reaction to obtain the SUS mesh-framed, gel electrolyte-embedded NCM811 cathode (fs-cathode). To prepare the fs-Li anode, the bottom side of the conductive PET nonwoven was preferentially coated with lithiophilic Ag thin layers using a sputter deposition method. Subsequently, Li was deposited into the obtained Ag-cPET nonwoven using an electrochemical plating process. For the electrochemical plating, 2032-type coin cells (cPET/Ag || Li metal foil) were employed. The cells were cycled at 0.001 V to 3 V at 50 μA during the initial cycling to form stable solid electrolyte interphase layers on the Ag-cPET nonwoven. Subsequently, 5 mAh cm$^{-2}$ of Li was deposited into the Ag-cPET nonwoven.

### 2.4 Electrochemical characterization of the fs-QSSLMBs

To investigate the electrochemical performance of the fs-QSSLMBs, 2032-type coin cells were assembled in an Ar-filled glove box. To prevent the corrosion caused by LiFSI salts, Al-clad cases were used. The CE of the cell was estimated using Li foil || Ag-cPET and Li foil || Cu asymmetric cells, in which the thickness of the Li foil was 200 μm and 4 M LiFSI in PC/FEC was used as the electrolyte. For the symmetric cells (fs-Li || fs-Li and Li-plated Cu || Li-plated Cu), first, 5 mAh cm$^{-2}$ of Li was deposited at a current density of 0.5 mA cm$^{-2}$. Subsequently, 1 mAh cm$^{-2}$ of Li was repeatedly stripped and deposited at a current density of 1 mA cm$^{-2}$ during the galvanostatic cycling. The electrochemical performance of the fs-QSSLMB cells (fs-cathode with an areal mass loading of 14.7 mg cm$^{-2}$, which corresponds to an areal capacity of 2.8 mAh cm$^{-2}$) and fs-Li anode (with an areal capacity of 5 mAh cm$^{-2}$ and N/P ratio of 1.8) was evaluated under a voltage range of 3.0–4.2 V using a cycle tester (PNE Solution) at room temperature. The AC impedance of the cells was evaluated using a potentiostat/galvanostat (VSP classic, Bio-Logic).

### 3 RESULTS AND DISCUSSION

#### 3.1 PET nonwoven-framed QSSE membranes (fs-QSSE membranes)

The schematic illustration of the fabrication procedure of the PET nonwoven-framed QSSE (denoted as fs-QSSE) membrane is shown in Figure 1A. The QSSE paste consisted of a gel electrolyte precursor (composed of a non-flammable coordinated electrolyte (4 M lithium bis (fluorosulfonyl)imide [LiFSI] in propylene carbonate [PC]/fluoroethylene carbonate [FEC] = 93/7 [vol/vol])) and UV-curable ethoxylated trimethylolpropane triacrylate (ETPTA) monomer) and Al$_2$O$_3$ nanoparticles (average size ~300 nm), in which the composition ratio of the QSSE paste was 4 M LiFSI in (PC–FEC)/ETPTA (≈ 90/10 [wt/wt]) / Al$_2$O$_3$ = 50/50 (wt/wt). The Al$_2$O$_3$ nanoparticles were introduced into the QSSE to control the rheological properties of the QSSE paste and also act as a structural spacer to prevent internal short-circuit failure between electrodes.

The QSSE paste exhibited a typical shear-thinning fluid behavior\(^\text{25}\) (Figure S1A). In addition, the storage modulus (G') of the paste was higher than the loss modulus (G'') in the low shear stress range; however, a crossover of G' and G'' was observed in the high shear stress range, indicating that the paste exhibited a thixotropic fluid behavior, which is desirable for a stencil
printing process (Figure S1B). In addition, a porous PET nonwoven (thickness ~14 µm and porosity ~72%) with highly entangled fibrous networks (Figure S2) was used to act as a mechanical skeleton for the QSSE. The as-prepared QSSE paste was printed on a PET nonwoven, after which the paste was subjected to UV curing to obtain a self-standing flexible fs-QSSE membrane with uniform dispersion of Al₂O₃ nanoparticles (inset of Figure 1B and Figure S3). Fourier transform-infrared (FT-IR) analysis (Figure S4) revealed that the characteristic peak corresponding to the acrylic C=Ĉ bond of ETPTA disappeared after the UV curing, verifying the successful UV-driven curing of the ETPTA in the presence of the PET nonwoven. In addition, the thickness of the fs-QSSE membrane was approximately 30 µm (Figure 1B), which is remarkably thinner than those of previously reported inorganic solid-state electrolytes. The thin fs-QSSE membrane was expected to positively affect the volumetric energy density of the resulting SSLMB full cell.

The mechanical flexibility of the fs-QSSE membrane under various mechanical deformation modes was investigated (Figure 1C). The fs-QSSE membrane stably maintained its physical shape and structural integrity under multiple-folding and crumpling. Moreover, there was no significant change in the fs-QSSE membrane without any detachment of the QSSE from the PET nonwoven after 10,000 bending cycles (bending radius = 5 mm), indicating its excellent mechanical flexibility and interfacial robustness (Figure S5). In addition, scanning electron microscopy (SEM) revealed that neither cracks nor defects were formed in the deformed fs-QSSE membrane, confirming the mechanical flexibility and structural integrity of the membrane (Figure 1D). In comparison, a control sample (a QSSE membrane without the PET nonwoven) was easily broken in half after the 1st folding cycle (Figure S6). The mechanical flexibility of the fs-QSSE membrane was further examined by measuring its stress–strain behavior (Figure 1E). The modulus of the fs-QSSE membrane (18 MPa) was higher than that of
the control sample (0.75 kPa). These results demonstrate the advantageous effect of the PET nonwoven on the mechanical flexibility and thickness reduction of the resulting fs-QSSE membrane.

The electrochemical stability of the fs-QSSE membrane was examined using linear sweep voltammetry analysis (Figure S7). The fs-QSSE membrane showed good oxidation/reduction stability due to the coordinated Li$^+$-FSI$^-$ solvent clusters in the 4 M LiFSI-PC/FEC electrolyte. Moreover, the ionic conductivity of the fs-QSSE membrane was estimated in the temperature range of 25−80°C using electrochemical impedance spectroscopy (EIS) (Figure 1F). The fs-QSSE membrane exhibited a satisfactory ionic conductivity level (e.g., 2.0 × 10$^{-4}$ S cm$^{-1}$ at room temperature) over a wide range of temperatures. Furthermore, the ionic conductivity of the fs-QSSE membrane showed superior thermal tolerance (Figure S8) compared to a conventional liquid electrolyte (1 M LiPF$_6$ in ethylene carbonate [EC]/ethyl methyl carbonate = 50/50 [vol/vol]). In addition, the fs-QSSE membrane exhibited a nonflammable behavior (Figure 1G and Movie S1), whereas the conventional liquid electrolyte-impregnated polyethylene separator was easily combustible (inset of Figure 1G, and Movie S2).

The thermal stability of the fs-QSSE membrane was attributed to the nonflammable characteristic of the coordinated electrolyte (4 M LiFSI in PC/FEC).

3.2 | SUS mesh-framed, gel electrolyte-embedded NCM811 cathodes (fs-cathodes)

The SUS mesh-framed, gel electrolyte-embedded NCM811 cathode (fs-cathode) was fabricated using the UV curing-assisted printing process, and the schematic illustration of the fabrication process is shown in Figure 2A. To prepare the NCM811 cathode, the NCM811 active powders were mixed with the gel electrolyte precursor (4 M LiFSI in PC-FEC/ETPTA = 90/10 [wt/wt]) and carbon black additives at a composition ratio (NCM811/carbon black/gel electrolyte precursor) of 70/5/25 (wt/wt/wt). The resulting cathode paste exhibited a typical thixotropic fluid behavior (Figure S9).

The cathode paste with well-tuned rheological properties was printed on a SUS mesh and subjected to UV curing to obtain a self-standing flexible fs-cathode (an inset of Figure 2B). The SUS mesh (shown in Figure S10) was introduced to the cathode paste as a conductive

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**FIGURE 2** SUS mesh-framed, gel electrolyte-embedded NCM811 cathodes (fs-cathodes). (A) Schematic illustration of the fabrication procedure of the fs-cathode. (B) Surface SEM image of the fs-cathode. The inset shows a photograph of the self-standing flexible fs-cathode. (C) Photographs showing the physical appearance of the fs-cathode (top) and control cathode (bottom) before and after the multiple folding test. (D) Change in the relative electrical resistance ($R/R_o$) of the fs-cathode (vs. control cathode) as a function of longitudinal compression cycle (bending radius = 3 mm). The inset shows a photograph of the fs-cathode upon the bending deformation. SEM, scanning electron microscope.
fibrous skeleton. The characteristic peak corresponding to acrylic C=C bond of ETPTA was not observed in the FT-IR spectrum of the fs-cathode, confirming the successful UV curing of the ETPTA in the fs-cathode (Figure S11). In addition, the SUS mesh in the fs-cathode was compactly filled with the cathode components (i.e., NCM811 powders, carbon black, and gel electrolyte) (Figure 2B and Figure S12).

Owing to the presence of the SUS mesh, which acted as a mechanical skeleton, there was a significant enhancement in the mechanical flexibility of the fs-cathode compared to that of the control cathode (fabricated by casting a cathode slurry on an Al foil current collector). To better elucidate the superior flexibility of fs-cathode, the mechanical properties of the SUS mesh were compared with those of the Al foil current collector (Figure S13). The Al foil showed a low yield strain (~1.6%) and underwent irreversible plastic deformation. By comparison, the SUS mesh presented a high yield strain (~13%) owing to its well-established fibrous networks. In addition, compared to the control cathode which showed mechanical cracks, particularly, at the folded edges, the fs-cathode maintained its structural stability after multiple folding deformation (Figure 2C and Figure S14). This superior flexibility of the fs-cathode was further verified by monitoring the change in its electrical resistance as a function of the longitudinal compression cycle at a bending radius of 3 mm (Figure 2D). There was an abrupt increase in the electrical resistance of the control cathode, and the cathode was mechanically broken before 300 bending cycles. In contrast, there was no significant change in the electrical resistance of the fs-cathode even after 5000 bending cycles, indicating its excellent mechanical flexibility.

3.3 | Ag-coated conductive PET nonwoven-framed Li metal anodes (fs-Li anodes)

A recent study explored the use of the Cu/Ni-deposited conductive PET nonwoven as flexible Li metal anodes. Inspired by the results of the previous study, we exploited the use of conductive PET nonwoven as a mechanical skeleton for Li metal anodes. To improve the lithiophilicity of the conductive PET nonwoven, the bottom side of the conductive PET nonwoven was preferentially coated with lithiophilic Ag thin layers using a sputter deposition method. The surface morphology of the obtained Ag-coated conductive PET (Ag-cPET) nonwoven is shown in Figure S15. The Ag thin layer preferentially deposited at the bottom side of the PET nonwoven enabled the formation of a lithiophilic-gradient morphology in the resulting Ag-cPET nonwoven, which is known to facilitate the bottom-up plating of Li in 3D Li hosts. Subsequently, Li was introduced into the framework of the Ag-cPET nonwoven using an electrochemical plating process to obtain an Ag-coated conductive PET nonwoven-framed Li metal anode (fs-Li anode) (Figure 3A), of which the detailed experimental procedure is described in the experimental section.

Compared to a pristine Cu (~75 mV), the Ag-cPET nonwoven exhibited a significantly reduced Li nucleation overpotential (~15 mV) at a current density of 0.5 mA cm$^{-2}$ (Figure 3B), which could be attributed to its high surface area (that can reduce local current density) and the Ag thin layer-driven lithiophilic-gradient morphology. Consequently, the Ag-cPET nonwoven enabled the uniform nucleation and growth of Li, thus facilitating the formation of a thin-film fs-Li anode (thickness ~52 μm and areal capacity = 5 mAh cm$^{-2}$) with densely-deposited Li (Figure S16). To evaluate the Li plating/stripping reversibility of the Ag-cPET, the Coulombic efficiency (CE) of an Ag-cPET || Li cell was compared to that of a Cu foil || Li cell at a current density of 1 mA cm$^{-2}$ and an areal capacity of 1 mA cm$^{-2}$ (Figure 3C). The Ag-cPET || Li cell exhibited a stable and high CE during cycling, whereas the CE of the Cu foil was severely unstable and fluctuating, demonstrating the superior Li plating/stripping cyclability of the Ag-cPET. Moreover, compared to a Li-plated Cu (5 mA cm$^{-2}$) || Li-plated Cu (5 mA cm$^{-2}$) symmetric cell, which exhibited a voltage fluctuation before 450 h, a fs-Li (5 mA cm$^{-2}$) || fs-Li (5 mA cm$^{-2}$) symmetric cell exhibited a stable cycle retention without any significant increase in its overpotential (Figure 3D).

The mechanical flexibility of the fs-Li anode was investigated by measuring the change in its electrical resistance as a function of the longitudinal compression cycle at a bending radius of 3 mm (Figure 3E). There was no significant change in the electrical resistance of the fs-Li anode even after 3000 bending cycles, whereas there was a sharp increase in the electrical resistance of the Li-plated Cu just before 500 bending cycles, which is similar to the reports of previous studies. In addition, to further verify the superior flexibility of fs-Li anode, the mechanical property of the Ag-cPET was compared with that of the Cu foil current collector (Figure S17). The Cu foil showed a low yield strain (~1%) along with the irreversible plastic deformation. In contrast, the SUS mesh presented a high yield strain (~30%) owing to its well-developed fibrous networks. These results demonstrate that the Ag-cPET nonwoven played a crucial role in improving the Li plating/stripping reversibility and mechanical flexibility of the anode, indicating its viability as a multifunctional flexible 3D Li host.
3.4 Quasi-solid-state Li metal full cells with seamless interfaces (fs-QSSLMB)

The fs-QSSLMB was fabricated using a stepwise printing, followed by UV curing (Figure 4A). The simplicity and effectiveness of the printing technique for cell fabrication were reported in our previous studies. To fabricate the cell, first, a cathode paste was embedded into a SUS mesh using a stencil printing process. Thereafter, a PET nonwoven was placed in the SUS mesh-embedded cathode paste, after which a QSSE paste was introduced using the stencil printing process. Subsequently, a fs-Li anode was placed on top of the QSSE paste/cathode paste. Last, the fs-Li anode/QSSE paste/cathode paste assembly was subjected to UV irradiation to obtain a fs-QSSLMB. The overall fabrication procedure is schematically illustrated in Figure S18. The stepwise printing process combined with the one-pot UV curing applied for the fabrication of the fs-Li anode/QSSE paste/cathode paste assembly enabled the formation of seamless interfaces between the electrodes and QSSE (Figure 4B), which reduced the interfacial resistance of the fs-QSSLMB. A control QSSLMB cell was fabricated by simply stacking the individually prepared cell components (i.e., fs-Li anode sheet, QSSE membrane, and fs-cathode sheet).

Compared to the control QSSLMB (~320 Ω), the fs-QSSLMB exhibited a lower cell resistance (~80 Ω),
demonstrating the advantageous effect of the seamless interfaces (Figure 4C). In addition, the fs-QSSLMB maintained its structural integrity upon exposure to bending deformation (Figure S19), whereas the electrodes and QSSE membrane were easily detached in the control QSSLMB (Figure S20). These results demonstrate the viable role of the seamless interfaces in achieving the lower cell resistance and mechanical flexibility of the fs-QSSLMB.

The electrochemical performance of the fs-QSSLMB cell (fs-cathode (areal mass loading of 14.7 mg cm$^{-2}$, corresponding to an areal capacity of 2.8 mAh cm$^{-2}$) and fs-Li anode (areal capacity of 5.0 mAh cm$^{-2}$ and N/P ratio of 1.8) was investigated at a charge/discharge current density of 0.1 C/0.1 C. The fs-QSSLMB showed a normal charge/discharge profile at the 1st cycle and a discharge capacity of 180 mAh g$^{-1}$ with an initial CE of 99.6% (Figure 4D). Furthermore, the fs-QSSLMB exhibited a stable cycling performance (at charge/discharge current densities of 0.1 C/0.1 C [Figure 4E] and 0.5 C/0.5 C [Figure S21]) and a fast discharge rate capability (measured at a fixed charge current density of 0.1 C, Figure 4F).

Moreover, compared to previously reported flexible solid-state LMBs, the fs-QSSLMB exhibited a high...
areal mass loading of cathode materials (14.7 mg cm\(^{-2}\)) and high areal capacity (2.6 mAh cm\(^{-2}\)), (Figure 4G and Table S1). To further verify the superior electrochemical performance of the fs-QSSLMB, its gravimetric/volumetric energy densities were compared with those of previously reported flexible solid-state LMBs\(^{38-47}\) (Figure 4H and Table S2), in which the gravimetric and volumetric energy densities were expressed as Wh kg\(_{\text{cell}}^{-1}\) and Wh L\(_{\text{cell}}^{-1}\), respectively (the weight and volume of the cell, including those of the anode, cathode, and electrolyte). The fs-QSSLMB exhibited remarkably high energy densities (385 Wh kg\(_{\text{cell}}^{-1}\)/451 Wh L\(_{\text{cell}}^{-1}\)), which were significantly higher than those of previously reported flexible solid-state LMBs.

3.5 | Mechanical flexibility and safety of the fs-QSSLMB

The mechanical flexibility and safety of the fs-QSSLMB were investigated using a pouch-type cell (width/length/thickness = 30/30/160 [mm/mm/μm]). The fs-QSSLMB was mechanically folded under various folding angles of 0, 45, 135, and 180°, after which the cell performance was examined at a charge/discharge current density of 0.1 C/0.1 C. The fs-QSSLMB showed normal charge/discharge profiles over wide ranges of folding angles. In addition, there was no significant change in the discharge capacity of the fs-QSSLMB even at a folding angle of 180° (Figure 5A).

**FIGURE 5** Mechanical flexibility and safety of the fs-QSSLMB. (A) Charge/discharge profiles of the fs-QSSLMB at various folding angles of 0, 45, 135, and 180° at a charge/discharge current density of 0.1 C/0.1 C. (B) Change in the discharge capacity (measured at a charge/discharge current density of 0.1 C/0.1 C) of the fs-QSSLMB under repeated folding/unfolding cycles (at a folding angle of 180°). (C) FEA of the stress evolution of the control QSSLMB (I), (II), and fs-QSSLMB upon mechanical deformation. (D) Safety test of the fs-QSSLMB: initial state (left), after being vertically cut in half (middle), and upon exposure to flame (right). FEA, finite element analysis; fs-QSSLMB, fibrous skeleton-framed, quasi-solid-state LMB; LMB, lithium-metal battery.
Moreover, the fs-QSSLMB exhibited a stable capacity retention under repeated folding/unfolding cycle (at a folding angle of 180°) (Figure 5B). In addition to the folding test, the fs-QSSLMB was wound along a rod (radius = 5 mm). Under this deformed state, the fs-QSSLMB exhibited normal charge/discharge profiles (Figure S22). These results can be attributed to the combined effect of the fibrous skeletons and seamless interfaces on the mechanical deformability of the fs-QSSLMB.

The superior mechanical deformability of the fs-QSSLMB was verified by simulating the stress evolution of the cell upon mechanical deformation using a finite element analysis (FEA) software (Figure 5C). The detailed information of the simulation factors is listed in Table S3. To highlight the outstanding properties of the fs-QSSLMB, two control QSSLMBs were prepared. Control QSSLMB (I) consisted of a conventional slurry-cast cathode (containing an Al current collector), a Li metal anode (with a Cu current collector), and a fs-QSSE membrane. Control QSSLMB (II) was fabricated by simply stacking the individually prepared cell components, including the fs-Li anode sheet, QSSE membrane, and fs-cathode sheet. The control QSSLMB (II) showed a lower stress evolution than the control QSSLMB (I), demonstrating the advantageous effect of the fibrous skeletons embedded in the electrodes on the mechanical flexibility of the cell. In addition, compared to the control QSSLMBs (I) and (II), the stress evolution in the fs-QSSLMB was alleviated. This result confirms the combined effect of the seamless interfaces and fibrous skeletons in suppressing the internal stress evolution of the fs-QSSLMB.

The safety of the fs-QSSLMB was investigated by observing its electrochemical activity under harsh operating conditions (Figure 5D and Movie S3). The fs-QSSLMB continuously powered a light-emitting diode (LED) lamp after being cut into two pieces. Furthermore, the halved fs-QSSLMB operated the LED lamp even upon exposure to flame. The enhancement in the safety of the fs-QSSLMB was mainly attributed to the nonflammability and thermal stability of the QSSE (Figure 1G).

4 | CONCLUSION

We have presented a fs-QSSLMB as a new cell architecture concept to simultaneously achieve the high-energy-density, mechanical flexibility, and safety. The incorporation of the fibrous skeletons (SUS mesh for the NCM811 cathode, PET nonwoven for the QSSE, and Ag-c-PET nonwoven for the Li metal anode) into the fs-QSSLMB improved the structural integrity and mechanical flexibility of the cell. In addition, the stepwise printing of the NCM811 cathode/QSSE/Li anode assembly and the subsequent one-pot UV curing of the gel electrolyte precursors in the assembly enabled the formation of seamless interfaces between the electrodes and QSSE, which played a viable role in the electrochemical sustainability and mechanical deformability of the fs-QSSLMB. Furthermore, the fibrous skeleton-based structural uniqueness and seamless interfaces of the fs-QSSLMB enabled the high areal capacity, cycling stability, and high (cell-based) gravimetric/volumetric energy densities (385 Wh kg\(^{-1}\)/451 Wh L\(^{-1}\)) of the cell, which were significantly higher than those of previously reported solid-state flexible LMBs. Moreover, there was a significant enhancement in the mechanical flexibility and safety (electrochemically active even after being vertically cut in half and exposed to flame) of the fs-QSSLMB. The findings of this study demonstrate the promising potential of the fs-QSSLMB as a facile and scalable cell architecture platform for practical flexible high-energy-density SSLMBs, which can be extended to other emerging metal battery systems (including zinc, magnesium, and aluminum batteries).

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

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