

3D-Printed Nanostructured Copper Substrate Boosts the Sodiated Capability and Stability of Antimony Anode for Sodium-Ion Batteries

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Sodium-ion batteries (SIBs) represent a viable substitute to lithium-ion batteries due to their affordability and resource abundance. For SIBs, antimony (Sb) shows potential as anode material but is impeded by the high volumetric variations. Here the challenges of Sb sodium storage by introducing the nanostructured Cu substrate for enhanced Sb adhesion and morphology optimization is addressed, which is realized by fused deposition modeling (FDM) printing of Cu substrate, subsequent high-temperature sintering, and electrodeposition of Sb. In SIBs, the Sb deposited on three dimensional (3D) printed Cu substrate performs improved cycling stability compared with that of Sb@Cu with commercial Cu foil substrate, which can be attributed to the nanostructure of the 3D-Cu substrate. Such architecture of 3D-Cu induces the generation of pine-leaf-like Sb clusters to promote stability and kinetics, and it aids the adhesion between the Sb cluster and 3D-Cu substrate for preventing the Sb detachment and restructuring the Sb cluster to the robust porous ligament-channel Sb framework. The morphology evolution, (de)sodiation mechanism, and gas evolution are explored by *ex situ* scanning electron microscope, *operando* X-ray diffraction, and *operando* differential electrochemical mass spectrometry separately. The developed Sb@3D-Cu anode offers a flexible pathway for constructing 3D-printed self-supported electrodes for SIBs.

generation systems based on renewable sources (such as hydraulic, tidal, solar power, etc.), have stimulated enormous scientific exploration for grid-scale energy storage systems (ESSs) to smoothly integrate sustainable energies into the power grid.^[1] Sodium-ion batteries (SIBs) have garnered significant interest as a potential replacement for lithium-ion batteries (LIBs) in ESSs, which derives from the obstacles targeting the production of Li and the abundant reserves and appropriate working potential of Na.^[2] Particularly, among the various anode materials, antimony (Sb) has been regarded as a potential candidate thanks to its impressive theoretical gravimetric capacity (660 mAh g⁻¹).^[3] Noticeably, Sb possesses decent electronic conductivity (2.4×10^6 S m⁻¹ at 20 °C) stemming from its semi-metallic characteristic and also contains plentiful vacant spaces to provide abundant channels for Na⁺ diffusion because of its layered structure with high *c*-axis value and low atomic packing parameter.^[4] Nevertheless, the exact electrochemical performance of the Sb anode is seriously

1. Introduction

Due to the increasing concerns of environmental issues and forthcoming fossil fuel exhaustion, decarbonized energy

limited by the unstable surface electrolyte interphase (SEI) upon the cycling, giving rise to the significant volumetric variation and structural failure primarily attributed to the larger atomic radius of Na⁺.^[3,5]

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To tackle this limitation, the emphasis is placed on nanoengineering the porous architecture,^[6] multi-metallic strategy,^[7] and hybridization with carbon materials,^[8] which can efficiently improve the ion and electron transportation and cushion the volume changes. Nonetheless, implementing these strategies on an industrial scale poses challenges due to the intricate fabrication processes, volume capacity reduction through introducing inactive metallic or carbonaceous components, and elevated costs.^[9] At the same time, the conventional slurry-casting method reduces gravimetric as well as volumetric capacities due to the inclusion of binders and conductive components. On the contrary, electrodeposition enables the fabrication of active materials on conductive substrates free from conductive additives and binders. This method yields electrodes with high tap density, and optimal electrical connectivity toward the substrate, and avoids any reduction in gravimetric and volumetric capacity without the addition of extra materials.^[10] However, prior research has highlighted the limited lifespan of electrodeposited Sb films. This issue is ascribed to the insufficient mechanical interaction between the Sb layer and substrate, which is unable to withstand the substantial volume fluctuations of Sb and thus leads to the pulverization and aggregation of Sb.^[11] Therefore, it is imperative to implement interface modulation to tackle the aforementioned matters and boost the electrochemical ability of electrodeposited Sb electrodes.

Three dimensional (3D) printing, as a cutting-edge method of additive manufacturing, is capable of producing on-demand self-supported electrodes with precise and flexible geometric and structural control.^[12] Among the diverse 3D printing approaches, fused deposition modeling (FDM) 3D printing has garnered significant attention as a rapid bottom-up manufacturing approach for producing electrodes in the field of electrochemistry (such as rechargeable batteries,^[13] supercapacitors^[14]), stemming from its eco-friendliness, simplicity, superior efficiency, low expense, as well as accurate and facile control over large size pieces.^[15] For the 3D printing of metals, it is worth noting that, compared with the traditional selective laser melting (SLM) technology requiring sophisticated equipment,^[16] FDM can significantly reduce the production cost based on the easily accessible metal-polymer filaments and simple conditions.^[17] Recently, FDM 3D printing with Cu-based filaments has aroused an emerging interest in printing 3D Cu substrate with targeted geometric shapes, sizes, and controllable morphology which was successfully applied to various electrochemical fields including electrocatalytic biosensing,^[18] water splitting,^[19] ammonia electrosynthesis,^[20] bio-recognition.^[17b] Inspired by the above-mentioned works, FDM 3D printing would be a facile way to improve the electrodeposited Sb/Cu current collector interfacial property and thus boost the electrochemical performance of self-supported Sb anode in SIBs via efficiently tailoring the nanostructure of the 3D-Cu substrate. However, so far such a method has not been used for fabricating substrate for Sb anode in SIBs to our best knowledge.

Therefore, in this work, Sb@3D-Cu electrode with nanostructured Cu substrate was prepared by FDM 3D printing and post-printing treatment (sintering and electrodeposition), which is of facile scalability deriving from the superior expandability of FDM 3D printing technique. In SIBs, the Sb@3D-Cu anode delivers significantly improved cycling stability, as benchmarked with that

of the Sb@Cu electrode using a commercial Cu foil substrate. Such enhanced sodiated storage capability can be attributed to the nanostructure of the 3D-Cu substrate. It not only induces the formation of pine-leaf-like Sb clusters with self-assembled nanosized Sb rods to achieve the decent integrity and kinetics of the Sb layer, but also enhances the adhesion between the Sb cluster and 3D-Cu substrate for impeding the aggregation of Sb and guiding the transformation of the pine-leaf-shaped Sb clusters into a mechanically robust porous ligament-channel Sb framework. This research provides an effective fabrication route for self-supported Sb anode, promoting the utilization of Cu 3D printing for SIBs.

2. Results and Discussion

Figure 1a and **Figure S1** (Supporting Information) schematically demonstrate the preparation of the Sb@3D-Cu electrode, and the in-depth details are given in the experimental section. In a typical procedure, the as-printed 3D-Cu electrodes are printed out utilizing the commercial Cu/poly(lactic acid) (PLA) filament (**Figure S1a**, Supporting Information). Subsequently, the sintering process is conducted to make the electrodes conductive via extracting PLA and sintering/consolidating the Cu particles within the filament. After sintering and treatment in HNO₃ solution, the electrode exhibits a bright copper color, implying the metallic surface of the electrode (**Figure S1b**, Supporting Information). Afterward, Sb is electrodeposited onto the 3D-Cu, creating a uniform black coating on the electrode's surface (**Figure S1c**, Supporting Information). Benefiting from the scalability and flexibility of 3D printing and electrodeposition, such procedure for Sb@3D-Cu is cost/time-effective and productive, easily scaling up to large areas. The X-ray diffraction (XRD) pattern (**Figure 1b**) of 3D-Cu is only indexed to the Cu (JCPDS # 65–9026) phase, further confirming the complete elimination of PLA during the sintering. Simultaneously, the XRD result (**Figure 1b**) of Sb@3D-Cu can be assigned to Sb (JCPDS # 35–0732) and Cu phases, demonstrating that the electrodeposited layer corresponds to pure Sb.

The scanning electron microscope (SEM) results (**Figure 1c,d**) of 3D-Cu demonstrate that the 3D-Cu displays a rugged and arcuated surface consisting of tightly connected Cu microparticles (**Figure 1c**). Notably, the surface of these Cu microparticles is composed of densely arrayed inclined nanocolumns with diameters of hundreds of nanometers (**Figure 1d**). The SEM images (**Figure 1e,f**; **Figure S2**, Supporting Information) of Sb@3D-Cu present that the pine-leaf-like Sb clusters are comprised of the self-assembled nanosized Sb rods with diameters of ≈ 30 nm, and homogeneously grown onto the 3D-Cu substrate with a thickness of 2.6 ± 0.5 μm (**Figure S2d**, Supporting Information). In contrast, the Sb clusters of Sb@Cu show large dimensions with the coarsened Sb nanorods (diameter, ≈ 50 nm) attached to the micron-sized twisty Sb sheets, and uneven distribution on Cu foil (**Figure S3**, Supporting Information). Such improvement upon the Sb clusters for Sb@3D-Cu can be attributed to the nanostructures (Herein, densely arrayed inclined nanocolumns) on the 3D-Cu, providing more nucleation sites and thus efficiently guiding the uniform formation and refinement of the Sb clusters.^[21] The corresponding EDX results show the slight oxidation of surficial Cu in 3D-Cu (**Figure S4**, Supporting Information), and present a roughly uniform distribution of Sb on 3D-Cu substrate (**Figure S5b**, Supporting Information). The surface

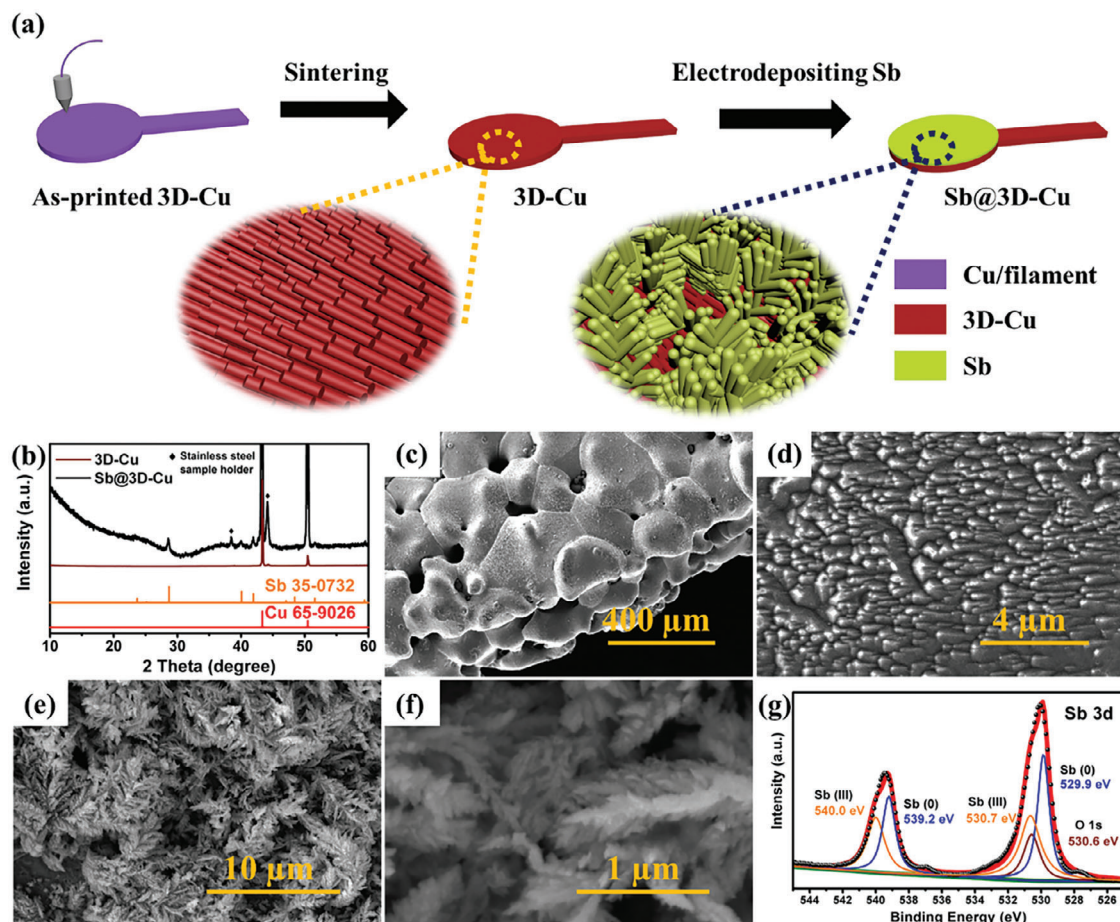


Figure 1. a) Schematic of the fabrication of Sb@3D-Cu. b) XRD patterns of 3D-Cu and Sb@3D-Cu. SEM micrographs of c, d) 3D-Cu and e, f) Sb@3D-Cu. g) Sb 3d XPS spectrum of Sb@3D-Cu.

chemical composition was assessed using X-ray photoelectron spectroscopy (XPS) analysis (Figure 1g; Figure S6, Supporting Information). The high-resolution Sb 3d XPS spectrum for Sb@3D-Cu (Figure 1g) reflects four distinct and well-defined signals, with peaks at 540.0/530.7 eV and 539.2/529.9 eV attributed to Sb (III) and Sb (0) states separately, indicating the presence of metallic Sb and Sb_2O_3 .^[6b,22] The high-resolution spectrum of Cu 2p for Sb@3D-Cu (Figure S6b, Supporting Information) exhibits three pairs of peaks, including 962.4/943.3 eV and 954.4/934.2 eV corresponding to Cu (II), as well as 952.0/932.1 eV belonging to Cu (0).^[23] The intensities of XPS peaks of Cu (0) are much higher than those of Cu (II), implying the low surficial oxidation degree of 3D-Cu, is consistent with the EDX results (Figures S6c and S4, Supporting Information).

Through cyclic voltammograms (CVs) and galvanostatic (dis)charge evaluations, the electrochemical capability of the Sb@3D-Cu electrode for SIBs was scrutinized. In Figure 2a, the CVs for the Sb@3D-Cu electrode, during its initial cycles, are showcased at a scan rate of 0.1 mV s⁻¹. Notably, in the cathodic scan, prominent peaks at 0.35/0.04 V (vs Na⁺/Na) are perceived, which is linked to the irreversible emergence of the solid-electrolyte interface (SEI) and sodiation process ($\text{Sb} \rightarrow \text{Na}_x\text{Sb} \rightarrow \text{Na}_3\text{Sb}$). In the anodic scan, the oxidation peak at

0.85 V (vs Na⁺/Na) represents the desodiation routine ($\text{Na}_3\text{Sb} \rightarrow \text{Na}_x\text{Sb} \rightarrow \text{Sb}$). After 5 cycles, the peaks located at 0.69/0.44 V (vs Na⁺/Na) as well as 0.84 V (vs Na⁺/Na) exhibit excellent overlap during the cathodic and anodic scans, indicative of adequate cycle stability. Figure S7 (Supporting Information) exposes the CVs of the Sb@Cu electrodes. The reduction peaks of Sb@Cu are positioned at 0.29/0.03 V (vs Na⁺/Na), showing a higher overpotential compared with those of 3D-Cu, thus implying its sluggish kinetics. Figure 2b displays the discharge as well as charge profiles of the Sb@3D-Cu electrode in various cycles under the current density of 1 A g⁻¹ (0.05, 0.2, and 0.5 A g⁻¹ for the 1st, 2nd – 6th, and 7th – 11th cycles). With respect to the 1st cycle, the discharge- as well as charge specific capacities can achieve values as high as 1142.1/471.9 mAh g⁻¹ accompanied by the initial Coulombic efficiency (ICE) of 41.3%. The significant irreversible capacity is attributed to the formation of the SEI layer during the initial cycle when the electrolyte interacts with the electrode surface.^[24] As depicted in Figure 2c, with cycling increasing, the discharge specific capacities gradually diminish and remain at 289.6 mAh g⁻¹ over 200 cycles. This performance significantly surpasses the cycling stability of Sb@Cu, which experiences rapid capacity degradation and plummets to only 57.3 mAh g⁻¹ after merely 10 cycles

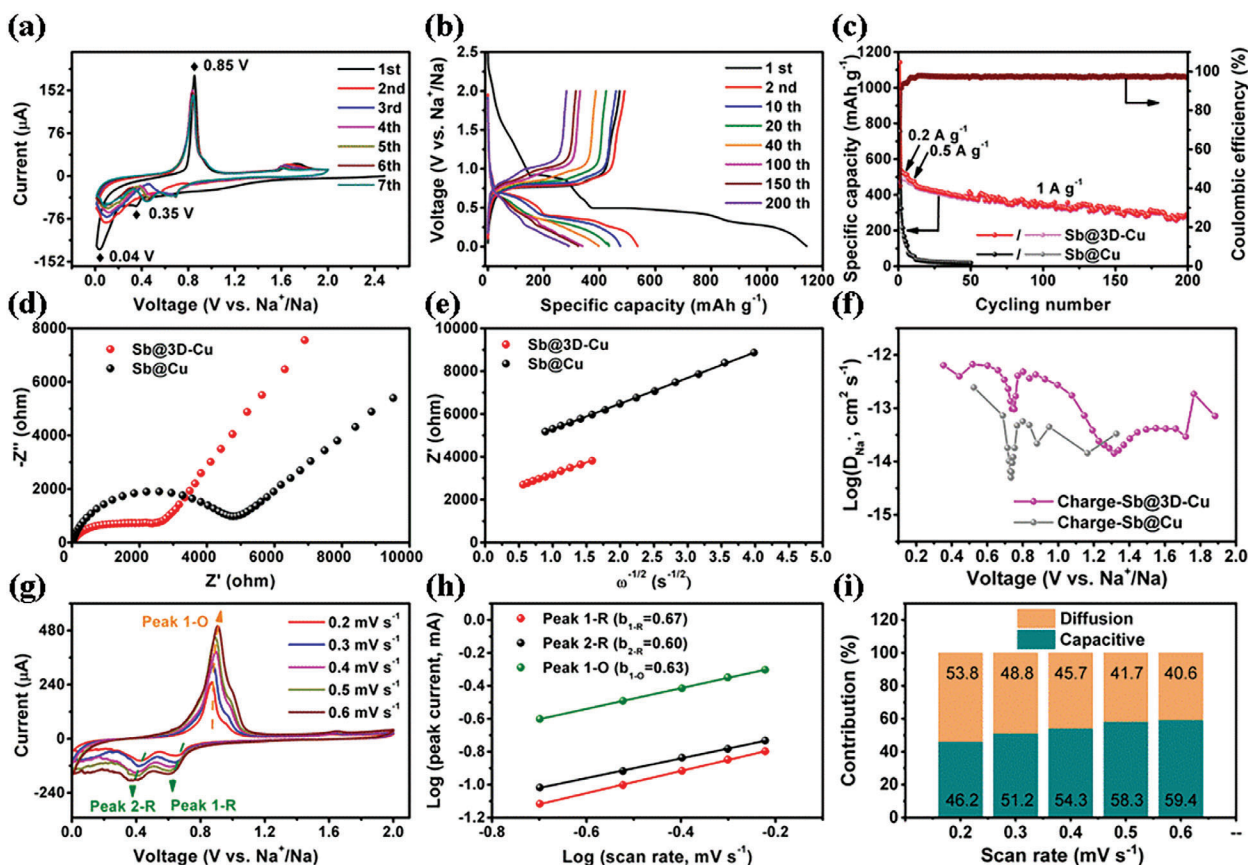


Figure 2. a) Cyclic voltammograms obtained at a scan rate of 0.1 mV s^{-1} , and b) the discharge/charge curves observed during various cycles at 1.0 A g^{-1} of the Sb@3D-Cu electrode. c) Cycling stability of the Sb@3D-Cu electrode, contrasted with that of the Sb@Cu electrode, both operated at 1.0 A g^{-1} . d) Nyquist diagrams, e) the correlation between Z'' and $\omega^{-1/2}$ within the low-frequency range at OCV. f) The Na^+ ions diffusion coefficient as a function of voltage derived from the GITT profiles (Figure S10, Supporting Information) during the second charging. g) CV curves of the Sb@3D-Cu electrode recorded at varying scan rates of 0.2, 0.3, 0.4, 0.5, and 0.6 mV s^{-1} over the potential range of 0.01–2.0 V (vs Na^+/Na). h) The linear correlation between $\log i$ versus $\log v$. i) The capacitive contribution ratios at different scan rates for Sb@3D-Cu.

(Figure S8, Supporting Information). Electrochemical impedance spectroscopy (EIS) was conducted to furnish additional revelation into the charge transfer properties. In Figure 2d, Nyquist plots for the Sb@3D-Cu and Sb@Cu electrodes at OCV are presented, with the subsequent fitting of an equivalent circuit (Figure S9, Supporting Information). The Warburg factor was determined by examining the interplay between Z'' and $\omega^{-1/2}$ within the low-frequency domain (Figure 2e). This factor was then used to proceed with the computation of the diffusion coefficient of Na^+ ($D_{\text{Na-eis}}$) using the referenced equations,^[25]

$$Z' = R_{\text{ct}} + R_e + \sigma \omega^{-1/2} \quad (1)$$

$$D_{\text{Na-eis}} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_{\text{Na}}^2 \sigma^2} \quad (2)$$

In the equation, R , T , n , A , F , C_{Na} , ω , and σ are employed to represent parameters including the gas constant, absolute temperature, the number of electrons per molecule involved in the reaction, the surface area of the electrode (geometric surface area is utilized in this study), the Faraday constant, Na^+ concentration, angular frequency, and Warburg factor which pertains to

the slopes in Figure 2e, respectively. Based on the computed outcomes (Table S1, Supporting Information), compared with those (R_{ct} , 4267.0Ω ; $D_{\text{Na-eis}}$, $5.1 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$) of the Sb@Cu electrode, the Sb@3D-Cu electrode shows the significantly reduced R_{ct} (2049.0Ω) and enhanced $D_{\text{Na-eis}}$ ($6.1 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$). Such a phenomenon reflects the facile diffusion of ions for the pine-leaf-like Sb clusters, which are favorably formed on 3D-printed Cu surfaces with abundant nano-rod structures.

As depicted in Figure 2f and Figure S10 (Supporting Information), the galvanostatic intermittent titration technique (GITT) was applied for the Sb@3D-Cu as well as Sb@Cu electrodes. This involved the application of a brief 0.05 A g^{-1} current density pulse for 1800 s, succeeded by a subsequent 7200 s open-circuit interval, allowing ample time for complete relaxation and the attainment of equilibrium potentials during charging (Figure S10, Supporting Information). The Na^+ diffusion coefficient ($D_{\text{Na-gitt}}$) values at various voltages were computed using the second law of diffusion proposed by Fick, as expressed in the abbreviated equation below,^[26]

$$D_{\text{Na-gitt}} = \frac{4}{\pi \tau} \left(\frac{n_m V_m}{A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_r} \right)^2 \quad (3)$$

where τ (in s) is the duration of the pulse, n_m (in mol) and V_m (in $\text{cm}^3 \text{mol}^{-1}$) are the mole number and molar volume of Sb,^[27] A (in cm^2) is the interface area between the electrode and electrolyte. ΔE_r and ΔE_s represent the voltage variation during the current pulse and the equilibrium-state potential alteration, respectively (Figure S10c, Supporting Information). During the charge in the second cycle, the $D_{\text{Na-gitt}}$ values of the Sb@3D-Cu electrode are about one order of magnitude larger than those of Sb@Cu electrode, which is in line with the EIS analysis (Figure 2d). The diffusion characteristics of the Sb@3D-Cu electrode were further elucidated through CVs measurements conducted at varying scan rates (Figure 2g–i; Figure S11, Supporting Information). The apparent connection between peak current (i) and scan rate (v) adheres to a power-law equation expressed as $i = av^b$, where a as well as b are adjustable coefficients.^[28] The nature of the electrochemical response can be ascertained through the b value. A b -value of 0.5 points to reactions primarily governed by diffusion, while a b -value of 1.0 indicates behavior predominantly influenced by the surface. When $\log(i)$ versus $\log(v)$ plots are fitted, the derived b -values for peak 1-R, 2-R, and 1-O are calculated with values of 0.67, 0.60, and 0.63 (Figure 2h), separately, demonstrating the combined contributions from the diffusion- and surface-controlled reactions. At the same time, the precise capacitive contribution ($k_1 v + k_2 v^{1/2}$) can be ascertained by applying the succeeding equation.^[29]

$$i = k_1 v + k_2 v^{1/2} \quad (4)$$

The constants k_1 and k_2 can be determined by a plot of $iv^{-1/2}$ against $v^{1/2}$. As depicted in Figure 2i and Figure S11a–e (Supporting Information), the capacitive contribution increases progressively from 46.2% (0.2 mV s^{-1}) to 59.4% (0.6 mV s^{-1}). This trend underscores the predominant role of non-Faradaic processes under high current densities.

To assess the structural stability of Sb@3D-Cu, ex situ SEM was conducted on the Sb@3D-Cu and Sb@Cu electrodes after 50 cycles (Figure 3a–d). The porous ligament-channel architecture can be detected for the Sb@3D-Cu electrode (Figure 3a), and uniformly distributed on the 3D-Cu substrate (Figure 3b). The generation of this porous ligament-channel framework is significantly advantageous for improving the integrity and kinetics of the electrode. The enormous channels can enhance the electrolyte permeation, shorten the ion transportation pathway, and allocate additional space to accommodate volumetric expansion/contraction, while the ligaments can form a highly robust and conductive network, efficiently reducing the deformation and accelerating the electron transfer.^[7b,30] On the contrary, the serious pulverization and aggregation of Sb can be found in the Sb@Cu electrode (Figure 3c,d), showing its inferior stability. Notably, the Sb@Cu₁₅Si₄ nanowire array anode reported by Ryan and co-workers^[30d] showed a complete restructuring of the Sb shell to the mechanically robust porous interconnected Sb ligaments after cycling. Such phenomenon can be primarily attributed to the strong anchoring effect provided by the Cu₁₅Si₄ NWs, and the buffer zone to allow Sb to expand freely during potassiation/de-potassiation processes. Hence, the aforementioned findings affirm that the incorporation of the 3D-Cu substrate enables the establishment of strong adhesion at the interface of the Sb layer and the 3D-Cu substrate, and thus restruc-

tures the pine-leaf-like Sb cluster into the mechanically robust porous ligament-channel Sb structure during cycling. Figure 3e schematically illustrates the mechanism of structural refinement and improved adhesion strength during the electrodeposition of Sb via introducing a 3D-Cu substrate. During the nucleation stage, the densely arrayed inclined nanocolumns of 3D-Cu can provide abundant nucleation sites for Sb deposition, inducing the formation of refined Sb clusters and uniform deposition. Conversely, for the smooth surface of Cu foil, the electrodeposition of Sb intends to occur upon the randomly distributed defects, leading to uneven nucleation. Meanwhile, the higher current density under the same deposition voltage during the electrodeposition of Sb@Cu compared with that of Sb@3D-Cu (Figure S11f, Supporting Information) further enhances such unevenness via the deposition concentrated at the tip of the formed grains,^[31] and finally inhomogeneously form the micron-sized twisty Sb sheets. Noticeably, the nanostructure of 3D-Cu can extend the contact area to a greater extent and thus achieve stronger adhesion strength compared with that of Cu foil with planar contact.^[32]

Long-term ultrasonic treatment was carried out for the Sb@3D-Cu and Sb@Cu electrodes (Figure S12, Supporting Information). Following the ultrasonic process for 1 h, observable detachment of the Sb layer in the Sb@Cu electrode was noted. In contrast, the Sb layer in the Sb@3D-Cu electrode remained stable, providing additional confirmation of the enhanced mechanical adhesion between the Sb layer and Cu substrate in the Sb@3D-Cu electrode. The stress–strain curves were measured via the tensile tests to clarify the mechanical property of 3D-Cu, with the scenario of commercial Cu foil under the same dimension for the benchmark (Figure S13, Supporting Information). Notably, the tensile strength of 3D-Cu reaches 329.93 MPa, significantly higher than that (50.51 MPa) of commercial Cu foil. Such improvement can mitigate the risk of mechanical failure in the current collector during long-term operation, and thus avoid the external electronic transport problem followed by battery fading.^[33] The visible plastic deformation demonstrates that the 3D-Cu possesses a macroscopically ductile behavior, indicating its decent potential as an engineering material.^[34]

In contrast to other recently reported self-supported pure or carbon/copper-hybridized Sb anodes for SIBs, the Sb@3D-Cu electrode expresses commendable overall electrochemical capability, effectively striking a balance between specific capacity and stability even at comparatively high current densities (Figure S14, Supporting Information). When compared to the Sb@Cu electrode, the impressive performance of the Sb@3D-Cu electrode can be credited to the unique nanostructure of the 3D-Cu substrate. On the one hand, the densely arrayed inclined nanocolumns on the 3D-Cu can induce the formation of pine-leaf-like Sb clusters, of which self-assembled nanosized Sb rods can endure the volumetric expansion along with a reduction in the diffusion distance to facilitate the ion transportation. On the other hand, the nanostructure of the 3D-Cu substrate can achieve the robust adhesion between the Sb cluster and 3D-Cu substrate, not only impeding the pulverization and aggregation of Sb but also triggering a comprehensive restructuring process that transforms the pine-leaf-like Sb clusters into a mechanically robust porous ligament-channel Sb framework, primarily due to the strong anchoring effect.^[30d]

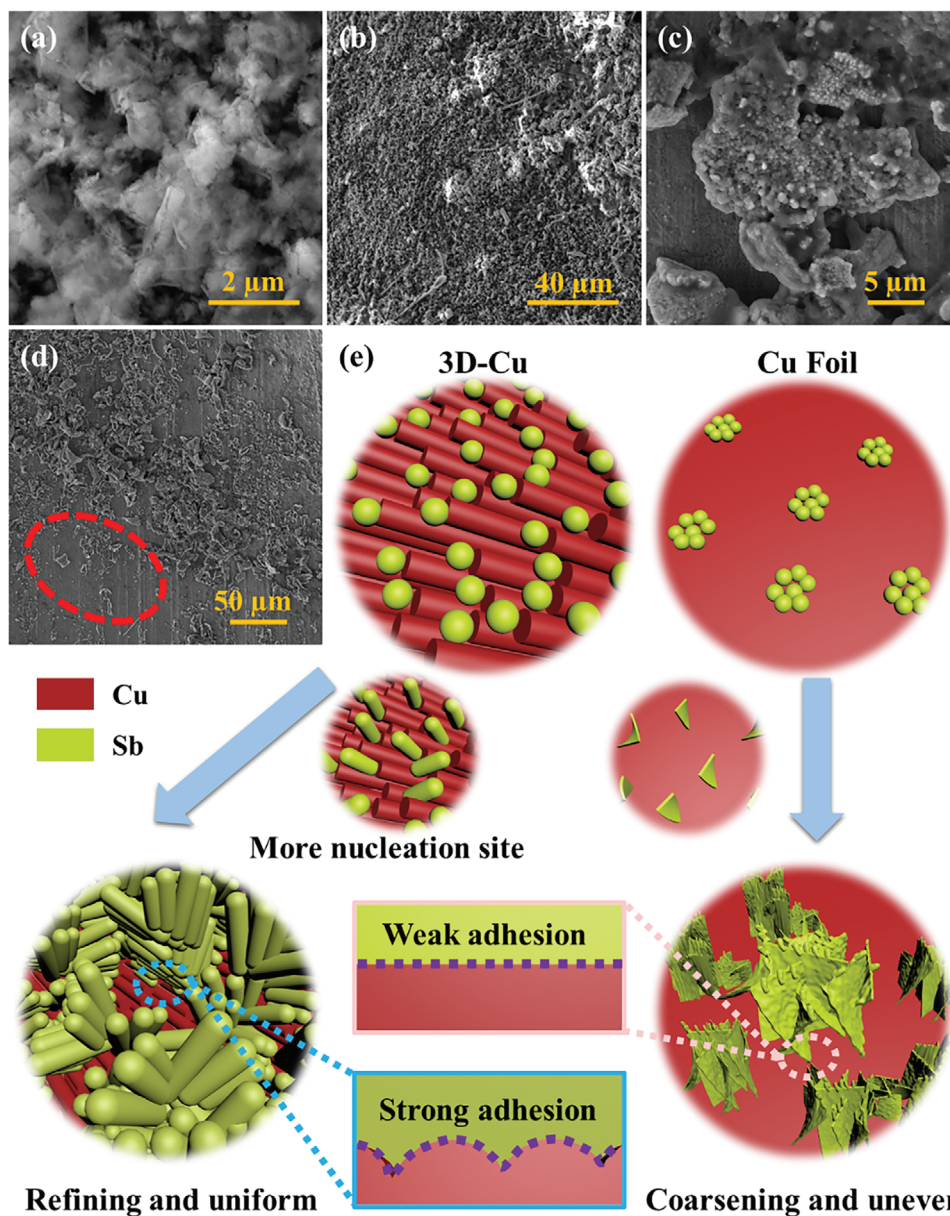
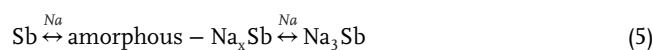


Figure 3. a–d) Ex situ SEM results of (a, b) Sb@3D-Cu and (c, d) Sb@Cu at 1 A g^{-1} after 50 cycles. e) Schematic demonstrating the electrodeposition mechanism of Sb for 3D-Cu and Cu foil.

In order to gain insight into the (de)sodiation mechanism of the Sb@3D-Cu electrode, operando XRD was conducted for real-time observation of phase changes throughout the first cycle (Figure 4a). In Stage 1 (OCV – 0.48 V (vs Na^+/Na)), the peaks occurring at $28.7^\circ/40.1^\circ/42.0^\circ$ associated with Sb progressively weaken without the presence of new peaks, revealing the emergence of a fully amorphous intermediate phase (Na_xSb) during the discharge stage.^[35] At the same time, the Sb peak at $\approx 28.7^\circ$ exhibits a slight shift toward lower angles, indicating the Na ion insertion into the Sb lattice within the initial stage of discharge.^[36] During the further sodiated procedure (Stage 2, 0.48–0.01 V (vs Na^+/Na)), the continuous formation of Na_3Sb (JCPDS # 65–3523) peaks at 21.3° , 33.4° , 34.2° , 42.7° , 43.3° , and 48.5° can be ob-

served, indicative of the sodiation of Na_xSb to form Na_3Sb . When subsequently reverted to 0.78 V (vs Na^+/Na) in Stage 3, the intensities of the Na_3Sb peaks gradually decrease and ultimately dissipate completely, indicating the desodiated transformation from Na_3Sb to Na_xSb . In Stage 4 (0.78–2.0 V (vs Na^+/Na)), the reappearance and consistent enlargement of the broad Sb peaks can be detected, indicating the desodiated process from Na_xSb to Sb and the elevated degree of amorphization for Sb. Thus, the (de)alloying mechanism of the Sb@3D-Cu electrode can be interpreted as follows.



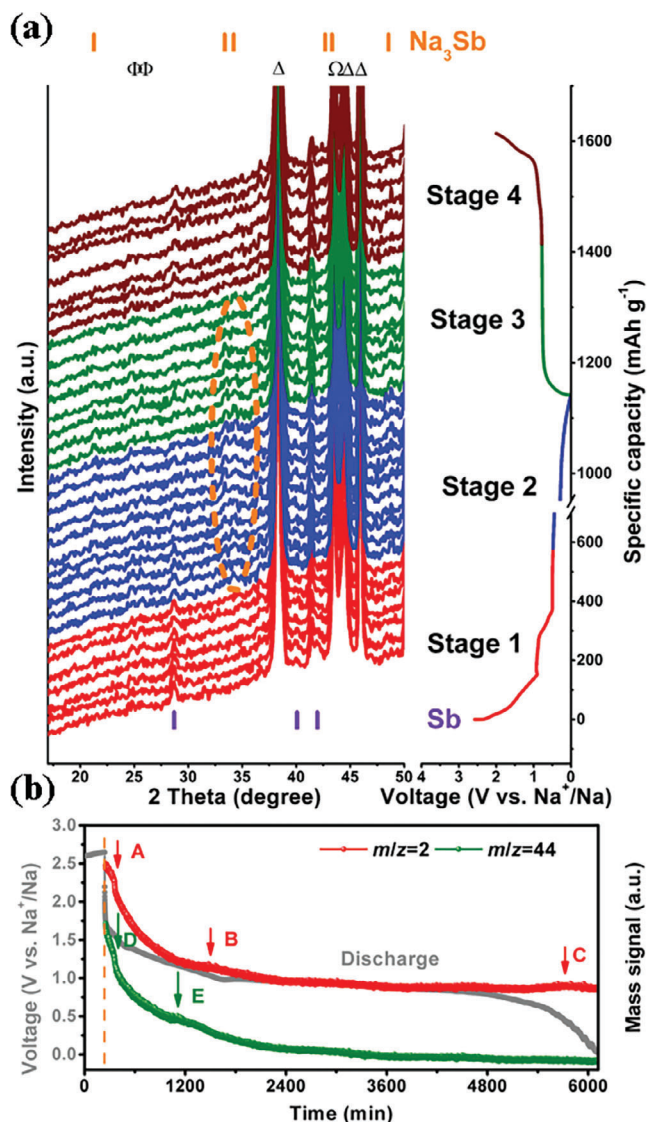


Figure 4. a) Operando XRD curves for the Sb@3D-Cu electrode within the 1st cycle for SIBs. The discharge as well as charge curves under the current density of 0.05 A g⁻¹ are also included as reference (right panel). The markers Δ, Φ, and Ω are used to represent BeO, Be₁₁Fe, and Cu, respectively. b) The operando DEMS outcomes from half-cells featuring the Sb@3D-Cu against metallic Na. The light gray line refers to the discharge curve within the range of 0.01–2.0 V (vs Na⁺/Na) at a current density of 0.05 A g⁻¹ for the 1st discharge.

Furthermore, operando differential electrochemical mass spectrometry (DEMS) was utilized for exploring gas generation and the interaction occurring at the interface between the electrode and the electrolyte during the initial discharge process of the Sb@3D-Cu electrode, while the signals corresponding to mass-to-charge (*m/z*) values of 2 and 44 were associated with hydrogen (H₂) and carbon dioxide (CO₂), respectively (Figure 4b). A mild release of H₂ (Peak A, B, and C) is observed during the initial discharge (from OCV to 1.0 V (vs Na⁺/Na)) and full discharged state, linked to the electrochemical reduction of minimal water in the electrolyte as well as a breakdown of the FEC

addition respectively.^[37] Simultaneously, the CO₂ release (Peaks D and E) is associated with the opening of the ring architecture of the PC solvent, resulting from the nucleophilic attack by hydroxide (OH⁻) anions produced from the reduction of water.^[38]

The Sb@3D-Cu electrode is further evaluated in a full cell coupled by a Na_{0.44}MnO₂ cathode. Figure S15a (Supporting Information) shows the charge–discharge profiles of the Sb@3D-Cu/Na_{0.44}MnO₂ full cell cycling between 1.6 and 3.2 V at the current density of 0.1 A g⁻¹. The full cell delivers an initial discharge capacity of 633.46 mA h g⁻¹ (based on the mass of anode) with a voltage plateau at ≈2.4 V, which is higher than those of MoO₃/Na₃V₂(PO₄)₃ (≈1.4 V)^[39] and FeSe₂/Na₃V₂(PO₄)₃ (≈1.7 V).^[40] Figure S15b (Supporting Information) shows the cycling performance of the Sb@3D-Cu/Na_{0.44}MnO₂ full cell. After 35 cycles, the discharge capacity remains 354.74 mA h g⁻¹. The capacity loss during cycling might be correlated with the formation of SEI film and the less match in the rate between the anode and cathode.^[41] In addition, the Sb@3D-Cu electrodes with higher mass loading of 10 mg cm⁻² (Sb@3D-Cu-10 mg) and 1 mg cm⁻² (Sb@3D-Cu-1 mg), were fabricated. The pronounced dissociation of surficial Sb is evident for Sb@3D-Cu-10 mg during the electrodeposition process (Figure S16a, Supporting Information), implying the weak stability within the upper layer of Sb clusters when the Sb clusters reach the critical size.^[42] Meanwhile, the Sb@3D-Cu-1 mg electrode delivers low reversible capacities with relative decent stability (Figure S16b, Supporting Information), not only further illustrating the reduced integrity within the upper layer of Sb clusters under elevated thickness which causes the Sb loss and low capacity, but also implying the robust structure within the bottom area of Sb clusters induced by 3D-Cu substrate which achieves the stable cycling.

3. Conclusion

A facile preparation of Sb@3D-Cu anode integrating FDM 3D printing and post-printing treatment which includes sintering and electrodeposition, is reported for SIBs. The nanostructure of the 3D-Cu substrate can not only guide the formation of pine-leaf-like Sb clusters with self-assembled nanosized Sb rods to realize the remarkable stability and kinetics of the Sb layer, but also strengthen the adhesion between the Sb cluster and 3D-Cu substrate for retarding the pulverization and aggregation of Sb and thus completely restructuring the pine-leaf-like Sb clusters into the mechanically robust porous ligament-channel Sb structure. Benefiting from these merits, the Sb@3D-Cu anode performs prominently improved cycling stability, outperforming that of the Sb@Cu electrode with commercial Cu foil substrate. This work provides a prototype of a 3D printing assisted self-supported anode for future SIBs.

4. Experimental Section

Material Fabrication: The 3D-printed electrodes were crafted using Autodesk Fusion 360, featuring a circular shape measuring 10 mm in diameter and 0.75 mm in thickness. Additionally, a connecting strip was included for linking with the working electrode during Sb electrodeposition. The design procedure document was processed using Prusa Slicer software, resulting in the generation of the corresponding G-code document. Subsequently, the 3D printing G-code file was executed using a printer (Prusa

i3, version: MK3). A commercially obtainable Cu/poly(lactic acid) (PLA) filament of the virtual foundry was employed. The printing process had a constant temperature of 215 °C for the brass nozzle (with a 0.6 mm diameter) and 60 °C for the bed. Subsequently, the as-printed 3D-Cu electrode underwent further sintering using a tube furnace with a N₂ condition. This process served to eliminate the poly(lactic acid) (PLA), facilitated the sintering of metallic copper microparticles, and ultimately enhanced electrical conductivity. The sintering process followed a specific heating ramp: Initially, it ramped up beginning from room temperature toward 300 °C at an elevated rate of 5 °C min⁻¹, then from 300 °C to 1010 °C at 3 °C min⁻¹, followed by a slower ramp from 1010 °C to 1075 °C at 1 °C min⁻¹. The sample was held at 1075 °C for 60 min and subsequently allowed to cool down gradually until it reached room temperature. Finally, the prepared electrodes were submerged in a 1 M HNO₃ solution and subjected to 15 min of bath sonication. This step was performed to eliminate surface impurities and produce the 3D-printed copper (3D-Cu) electrode.

For Sb electrodeposition, the circular disc portion of the 3D-Cu electrode was employed as the working electrode. It was placed into a mixed electrolyte comprising 0.05 M SbCl₃ and 0.15 M citric acid dissolved in ethylene glycol. The Sb electrodeposition was carried out within a three-electrode setup, with a platinum grid utilized as the counter electrode and an Ag/AgCl electrode (1 M KCl) used as the reference electrode. The formation of pine-leaf-like Sb structures on the 3D-Cu electrode occurred directly at a steady potential of -0.6 V (vs Ag/AgCl) with a cutoff charge of 0.309C. The resulting electrode was subsequently cleaned with ethanol and dried under ambient conditions. This process yielded the Sb@3D-Cu electrode having a mass loading of ≈0.2 mg cm⁻². Meanwhile, the Sb@3D-Cu-10 mg and Sb@3D-Cu-1 mg with higher mass loading of 10 and 1 mg cm⁻² were prepared by a similar method except for the cutoff charge (15.20 and 1.52 C), separately. For comparison, Sb@Cu electrodes were prepared using the same method, employing commercial Cu foil as the substrate.

Characterization: X-ray diffraction (XRD) measurements were conducted operating with a Rigaku SmartLab 3 kW diffractometer, employing Cu K α radiation ($\lambda = 1.54184$ Å). For microstructure analysis, scanning electron microscopy (SEM) was performed making use of a MIRA3-XMU instrument from a TESCAN electron microscope from the Czech Republic, with an electron beam acceleration voltage set at 10 kV. To determine chemical compositions, an energy-dispersive X-ray analyzer (EDX) equipped with an X-max20 detector was employed, operated at a 15 kV acceleration voltage. X-ray photoelectron spectroscopy (XPS) analysis was carried out operating a Kratos Analytical AXIS Supra instrument from Manchester, UK, employing monochromatized Al K α excitation with the value of 1486.7 eV. The acquisition of survey as well as high-resolution spectra was performed under the condition of the pass energies of 100 and 20 eV, respectively, while the binding energies were computed using the C 1s peak located at 284.8 eV. The CMT6103 electronic universal testing machine (SANS, Shenzhen, China) was utilized to measure the stress-strain curves of 3D-Cu and commercial Cu foil.

Electrochemical Measurements: The batteries were assembled in a Swagelok cell configuration, utilizing either the Sb@3D-Cu, Sb@3D-Cu-1 mg, or Sb@Cu as the working electrode. The electrolyte constituted 1 M sodium trifluoromethane sulfonimide (NaTFSI) dissolved in a solvent mixture containing propylene carbonate (PC) and fluoroethylene carbonate (FEC) with equal volumes (1:1). A glass fiber separator (Whatman GF/B) was applied, and sodium foil with purity of 99.8 wt.% (Sigma-Aldrich) served as the counter as well as reference electrodes. Battery assembly was manifested within the protective environment of an argon-filled glove box, and the assembled batteries were left to age for 24 h before testing. Electrochemical measurements were engaged within a voltage range of 0.01–2.0 V (vs Na⁺/Na). Galvanostatic tests and galvanostatic intermittent titration technique (GITT) method were employed utilizing a test system (LAND-CT2001A, Wuhan, China). Cyclic voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) tests were conducted using a potentiostat/galvanostat (AutoLab Metrohm PGSTAT204, Netherlands) linked to a computer equipped with Nova (Version: 2.1) software. EIS characterization was conducted at the open circuit voltage (OCV), covering a frequency with a limit from 10 mHz to 100 kHz and employing

an excitation potential of 5 mV. For the operando XRD, a custom-made CR2032 coin cell was used with a transparent Be window (10 mm in diameter) on one side for the X-ray analysis. It is important to note that the 3D-Cu substrate was punctured by a needle to generate closely spaced small openings (≈200 cm⁻²) for electrolyte permeation. XRD patterns were obtained using a “time step” mode at a current density of 0.05 A g⁻¹. Operando differential electrochemical mass spectrometry (DEMS) was conducted employing a custom cell based on the Swagelok design, consisting of two bonded capillary tubes with PEEK material for inlet and outlet of gas purging. This DEMS cell was connected to a commercial magnetic sector mass spectrometer (HPR-20 EGA, Hidden Analytical Ltd.) along with a purpose-built gas purging system that employed high-purity argon (99.999%) serving as a continuous flow of carrier gas and internal tracer gas. For post-cycling ex situ SEM characterization, the Sb@3D-Cu and Sb@Cu electrodes were disassembled after 50 cycles. They were meticulously cleaned using a diethyl carbonate (DEC) solution within the glove box and subsequently sealed in sample tubes for subsequent measurements. For the full cell, the Na_{0.44}MnO₂ cathode sheets were directly purchased from NEI Corporation with a mass loading of 8.55 mg cm⁻² (± 0.10 mg cm⁻²). The abovementioned Sb@3D-Cu electrode was utilized as the anode. The electrolyte used in the full cell was the same as that in the half cell, and the voltage window was fixed at 1.6–3.2 V.

Statistical Analysis: The thickness scale measurement was carried out with data presentation of mean ± SD via using Software Nano Measurer (Version 1.2.5) and measuring more than 100 points.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

additive manufacturing, anode, fused deposition modeling, operando X-ray diffraction, sodium ion battery

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- [1] B. Dunn, H. Kamath, J.-M. Tarascon, *Science* **2011**, 334, 928.
- [2] a) M. D. Slater, D. Kim, E. Lee, C. S. Johnson, *Adv. Funct. Mater.* **2013**, 23, 947; b) N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, *Chem. Rev.* **2014**, 114, 11636; c) J.-Y. Hwang, S.-T. Myung, Y.-K. Sun, *Chem. Soc. Rev.* **2017**, 46, 3529.
- [3] H. Tan, D. Chen, X. Rui, Y. Yu, *Adv. Funct. Mater.* **2019**, 29, 1808745.
- [4] a) M. Pumera, Z. Sofer, *Adv. Mater.* **2017**, 29, 1605299; b) S. M. Beladi-Mousavi, M. Pumera, *Chem. Soc. Rev.* **2018**, 47, 6964; c) K. Subramanian, V. Aravindan, *Chem* **2019**, 5, 3096; d) J. Sturla, Z. Sofer, M. Pumera, *Angew. Chem., Int. Ed.* **2019**, 131, 7631.
- [5] a) M. Lao, Y. Zhang, W. Luo, Q. Yan, W. Sun, S. X. Dou, *Adv. Mater.* **2017**, 29, 1700622; b) H. Zhang, I. Hasa, S. Passerini, *Adv. Energy Mater.* **2018**, 8, 1702582.
- [6] a) S. Liu, J. Feng, X. Bian, J. Liu, H. Xu, *Energy Environ. Sci.* **2016**, 9, 1229; b) W. Ma, J. Wang, H. Gao, J. Niu, F. Luo, Z. Peng, Z. Zhang, *Energy Stor. Mater.* **2018**, 13, 247.
- [7] a) J. Liu, Z. Yang, J. Wang, L. Gu, J. Maier, Y. Yu, *Nano Energy* **2015**, 16, 389; b) H. Gao, J. Niu, C. Zhang, Z. Peng, Z. Zhang, *ACS Nano* **2018**, 12, 3568; c) Y. Huang, Z. Wang, Y. Jiang, S. Li, M. Wang, Y. Ye, F. Wu, M. Xie, L. Li, R. Chen, *Adv. Sci.* **2018**, 5, 1800613.
- [8] a) Y. Zhao, A. Manthiram, *Chem. Mater.* **2015**, 27, 3096; b) Z. Liu, X.-Y. Yu, X. W. (D.) Lou, U. Paik, *Energy Environ. Sci.* **2016**, 9, 2314; c) X. Ou, C. Yang, X. Xiong, F. Zheng, Q. Pan, C. Jin, M. Liu, K. Huang, *Adv. Funct. Mater.* **2017**, 27, 1606242.
- [9] M. T. Demirkan, L. Trahey, T. Karabacak, *Thin Solid Films* **2016**, 600, 126.
- [10] J. Pu, Z. Shen, C. Zhong, Q. Zhou, J. Liu, J. Zhu, H. Zhang, *Adv. Mater.* **2020**, 32, 1903808.
- [11] M. C. Schulze, R. M. Belson, L. A. Kraynak, A. L. Prieto, *Energy Stor. Mater.* **2020**, 25, 572.
- [12] a) A. Ambrosi, M. Pumera, *Chem. Soc. Rev.* **2016**, 45, 2740; b) C. Zhu, T. Liu, F. Qian, W. Chen, S. Chandrasekaran, B. Yao, Y. Song, E. B. Duoss, J. D. Kuntz, C. M. Spadaccini, M. A. Worsley, Y. Li, *Nano Today* **2017**, 15, 107; c) M. P. Browne, E. Redondo, M. Pumera, *Chem. Rev.* **2020**, 120, 2783; d) J. Li, M. Pumera, *Chem. Soc. Rev.* **2021**, 50, 2794.
- [13] a) C. W. Foster, M. P. Down, Y. Zhang, X. Ji, S. J. Rowley-Neale, G. C. Smith, P. J. Kelly, C. E. Banks, *Sci. Rep.* **2017**, 7, 42233; b) Z. Lyu, G. J. H. Lim, J. J. Koh, Y. Li, Y. Ma, J. Ding, J. Wang, Z. Hu, J. Wang, W. Chen, Y. Chen, *Joule* **2021**, 5, 89.
- [14] a) X. Yan, Y. Tong, X. Wang, F. Hou, J. Liang, *Energy Environ. Mater.* **2022**, 5, 800; b) M. Li, S. Zhou, L. Cheng, F. Mo, L. Chen, S. Yu, J. Wei, *Adv. Funct. Mater.* **2023**, 33, 2208034.
- [15] a) S. Ng, C. Ifelsberger, Z. Sofer, M. Pumera, *Adv. Funct. Mater.* **2020**, 30, 1910193; b) W. Gao, M. Pumera, *Adv. Funct. Mater.* **2021**, 31, 2007285; c) W. Gao, J. Michalidika, M. Pumera, *Small* **2022**, 18, 2105572.
- [16] N. T. Aboulkhair, M. Simonelli, L. Parry, I. Ashcroft, C. Tuck, R. Hague, *Prog. Mater. Sci.* **2019**, 106, 100578.
- [17] a) S. Wickramasinghe, T. Do, P. Tran, *Polym* **2020**, 12, 1529; b) J. Muñoz, E. Redondo, M. Pumera, *Appl. Mater. Today* **2022**, 28, 101519.
- [18] E. Redondo, M. Pumera, *Appl. Mater. Today* **2021**, 25, 101253.
- [19] a) C. Ifelsberger, D. Rojas, M. Pumera, *J. Phys. Chem. C* **2022**, 126, 9016; b) J. Muñoz, C. Ifelsberger, E. Redondo, M. Pumera, *Appl. Catal. B* **2022**, 316, 121609.
- [20] J. V. Perales-Rondon, D. Rojas, W. Gao, M. Pumera, *ACS Sustainable Chem. Eng.* **2023**, 11, 6923.
- [21] L. Oniciu, L. Muresan, *J. Appl. Electrochem.* **1991**, 21, 565.
- [22] K.-S. Hong, D.-H. Nam, S.-J. Lim, D. Sohn, T.-H. Kim, H. Kwon, *ACS Appl. Mater. Interfaces* **2015**, 7, 17264.
- [23] D. Barreca, A. Gasparotto, E. Tondello, *Surf. Sci. Spectra* **2009**, 14, 41.
- [24] a) R. Fei, H. Wang, Q. Wang, R. Qiu, S. Tang, R. Wang, B. He, Y. Gong, H. J. Fan, *Adv. Energy Mater.* **2020**, 10, 2002741; b) T. Zhang, Z. Mao, X. Shi, J. Jin, B. He, R. Wang, Y. Gong, H. Wang, *Energy Environ. Sci.* **2022**, 15, 158.
- [25] a) Y.-R. Zhu, Y. Xie, R.-S. Zhu, J. Shu, L.-J. Jiang, H.-B. Qiao, T.-F. Yi, *Ionics* **2011**, 17, 437; b) D. Qu, G. Wang, J. Kafle, J. Harris, L. Crain, Z. Jin, D. Zheng, *Small Methods* **2018**, 2, 1700342; c) J. Zhong, T. Wang, L. Wang, L. Peng, S. Fu, M. Zhang, J. Cao, X. Xu, J. Liang, H. Fei, X. Duan, B. Lu, Y. Wang, J. Zhu, X. Duan, *Nano-Micro Lett.* **2022**, 14, 50.
- [26] a) Y. Zhu, C. Wang, *J. Phys. Chem. C* **2010**, 114, 2830; b) Z. Shen, L. Cao, C. D. Rahn, C.-Y. Wang, *J. Electrochem. Soc.* **2013**, 160, A1842; c) X. Huang, J. Zhao, W. Zhu, M. Hou, T. Zhou, L. Bu, L. Gao, W. Zhang, *J. Energy Chem.* **2021**, 63, 376.
- [27] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K. A. Persson, *APL Mater.* **2013**, 1, 011002.
- [28] J. Wang, J. Polleux, J. Lim, B. Dunn, *J. Phys. Chem. C* **2007**, 111, 14925.
- [29] a) G. Wang, N. Chandrasekhar, B. P. Biswal, D. Becker, S. Paasch, E. Brunner, M. Addicoat, M. Yu, R. Berger, X. Feng, *Adv. Mater.* **2019**, 31, 1901478; b) M. Chen, W. Hua, J. Xiao, D. Cortie, W. Chen, E. Wang, Z. Hu, Q. Gu, X. Wang, S. Indris, S.-L. Chou, S.-X. Dou, *Nat. Commun.* **2019**, 10, 1480.
- [30] a) Q. Chen, K. Sieradzki, *Nat. Mater.* **2013**, 12, 1102; b) T. Kennedy, E. Mullane, H. Geaney, M. Osiak, C. O'dwyer, K. M. Ryan, *Nano Lett.* **2014**, 14, 716; c) S. Imtiaz, I. S. Amiin, D. Storan, N. Kapuria, H. Geaney, T. Kennedy, K. M. Ryan, *Adv. Mater.* **2021**, 33, 2105917; d) S. Imtiaz, N. Kapuria, I. S. Amiin, A. Sankaran, S. Singh, H. Geaney, T. Kennedy, K. M. Ryan, *Adv. Funct. Mater.* **2023**, 33, 2209566.
- [31] J. Bu, J. Ru, Z. Wang, Y. Hua, C. Xu, Y. Zhang, Y. Wang, *Adv. Powder Technol.* **2019**, 30, 2859.
- [32] R. Liu, Y. Yuan, H. Wang, X. Guo, *Coatings* **2018**, 8, 201.
- [33] P. Zhu, D. Gastol, J. Marshall, R. Sommerville, V. Goodship, E. Kendrick, *J. Power Sources* **2021**, 485, 229321.
- [34] Y. Zhang, Q. Bai, W. Yang, Z. Zhang, *Sci. China Technol. Sci.* **2021**, 64, 2229.
- [35] A. Darwiche, C. Marino, M. T. Sougrati, B. Fraisse, L. Stievano, L. Monconduit, *J. Am. Chem. Soc.* **2012**, 134, 20805.
- [36] H. Gao, J. Lee, Q. Lu, Y. Kim, K. H. Shin, H. S. Park, Z. Zhang, L. Y. S. Lee, *Small* **2023**, 19, 2205681.
- [37] a) L. O. Vogt, M. El Kazzi, E. Jämsstorp Berg, S. Pérez Villar, P. Novák, C. Villevieille, *Chem. Mater.* **2015**, 27, 1210; b) F. Klein, R. Pinedo, B. B. Berkes, J. Janek, P. Adelhelm, *J. Phys. Chem. C* **2017**, 121, 8679; c) W. Liu, X. Chen, C. Zhang, H. Xu, X. Sun, Y. Zheng, Y. Yu, S. Li, Y. Huang, J. Li, *ACS Appl. Mater. Interfaces* **2019**, 11, 23207.
- [38] J. Ufheil, A. Würsig, O. D. Schneider, P. Novák, *Electrochem. Commun.* **2005**, 7, 1380.
- [39] S. Hariharan, K. Saravanan, P. Balaya, *Electrochem. Commun.* **2013**, 31, 5.
- [40] K. Zhang, Z. Hu, X. Liu, Z. Tao, J. Chen, *Adv. Mater.* **2015**, 27, 3305.
- [41] a) B. Qu, C. Ma, G. Ji, C. Xu, J. Xu, Y. S. Meng, T. Wang, J. Y. Lee, *Adv. Mater.* **2014**, 26, 3854; b) N. Wang, Z. Bai, Y. Qian, J. Yang, *Adv. Mater.* **2016**, 28, 4126.
- [42] S. C. S. Lai, R. A. Lazenby, P. M. Kirkman, P. R. Unwin, *Chem. Sci.* **2015**, 6, 1126.