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# Supporting Information

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**Supporting Information**

# Hierarchically Interpenetrated and Reentrant Micro-Cellular Frameworks for Stretchable Lithium Metal Batteries

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## Experimental Methods

*Materials*: Graphene oxide (GO) powder (GO-V50) with ~30 μm lateral size and ~1 nm thickness was purchased from Standard Graphene Inc. Single-walled carbon nanotubes (eDIPS EC1.5) with 90 % purity and 1-3 nm diameter were purchased from Meijo Nano Carbon Inc. Styrene-ethylene/butylene-styrene (SEBS, G1657MS) was obtained from Kraton Inc. $Ti_3AlC_2$ MAX powder (400 mesh, <38.0 μm particle size) was obtained from Carbon-Ukraine. The MXene was synthesized via a modified minimally intensive layer delamination (MILD) method, which involves removing aluminum (Al) from the $Ti_3AlC_2$ MAX phase using a solution made of LiF (> 99.99%, Sigma-Aldrich, Korea) and 6.0 M HCl (35-38.0%, Daejung Chemicals & Metals, Korea). The dispersed MXene nanosheet preparation was described in detail in our other paper.[39] Melamine foam was obtained from BASF Co. Ltd. Toluene (99%) was purchased from Daejung Chemical Co. Ltd. Lithium foil with 0.3 mm thickness was obtained from MTI Korea Co. Ltd. 1.0 M LiTFSi in DME/DOL (1:1 vol%) (Welcos Co. Ltd.) with 2wt% of $LiNO_3$ (99.999%, anhydrous, Alfa Aesar) were mainly used as an electrolyte. 1.0 M $LiPF_6$ in EC/DEC (1:1 vol%) with 7.5 wt% FEC electrolyte were purchased from Welcos Co. Ltd. For the Fenton reaction of the PVDF, PVDF (Mw ~ 534,000, powder, Sigma-Aldrich), $FeSO_4 \cdot 7H_2O$, hydrogen peroxide with 35 wt % were mixed in ethanol (Sigma-Aldrich), and reacted with 1 M $H_2SO_4$ (Daejung Chemical). $LiFePO_4$ (LFP, RD2121900A, Aleees Co., Ltd.) particles were used for the active materials of the cathode. For the stretchable current collector, 325 mesh Nickel flake (Alfa Aesar), 1 μm, and 50 μm Ni particles (Sigma-Aldrich), and a multi-walled carbon nanotube (MWCNT, length of 20−100 μm, average diameter of ~20 nm, purity >95 wt %, CNT Co., Ltd.) were purchased. Poly(styrene-*block*-isobutylene-*block*-styrene) (SIBS, 103T, Kaneka Corporation) was used as a matrix of the

stretchable current collector and a stretchable encapsulant. A stretchable separator was prepared using poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, average Mw ~ 400,000, pellets, Sigma-Aldrich).

*Preparation of GO, CNT, and MXene dispersion*: GO dispersion is prepared by mixing 105 mg of graphene oxide powder with 3.5 ml of water. After that, it is distributed to tip sonication with 40 % of amplitude and 04-01 s pulse for 30 min. CNT dispersion is prepared by mixing 150 mg of CNT with 30 ml of water. After that, it is distributed to tip sonication with 90 % of amplitude and 05-03 s pulse for 7 hr. Next, the MXene was dispersed in water (~25 mg/ml), and 2 ml of 1,4-Dioxane was added. Then, the GO, CNT, and MXene dispersions were mixed (weight ratio of the dispersants of 3.5:1.5:5) and stirred for 1 hr.

*Fabrication of Li-GCMMF electrode*: Melamine foam (MF) is cut to have a diameter of 30 mm and a thickness of 1 mm. The styrene-ethylene/butylene-styrene (SEBS) block copolymer was coated on the MF by immersing it in the SEBS solution (1 wt% in toluene) and drying by $N_2$ blowing. Then, the MF is immersed in the GO, CNT, and MXene dispersion solution and gently pressed to allow the dispersion to soak into the foam. The GO/CNT/Mxene dispersion soaked in MF is placed on a copper plate and directionally freezes over liquid nitrogen. After that, freeze-dry the foam to sublimate the directionally developed ice columns. Then, reduce GO/CNT/MXene-MF with hydrazine hydrate vapor for 24 hours on a hot plate at 80 ℃. After plating lithium on the reduced GCMMF, the Li-GCMMF with reentrant structures could be obtained through radial compression.

*Lithium electroplating*: For the electroplating method, the working electrode was the GCMMF electrode, and the counter electrode was a lithium metal foil. Electroplating was carried out using

a 100 ml beaker cell. Cells were assembled in the glove box below 0.1 ppm oxygen and water level. As the electrolyte, 1 M LiTFSI in 1,3-dioxolane and 1,2-dimethoxyethane (DOL:DME, volume ratio 1:1) with 2 wt% $LiNO_3$ was used. The charging rate was 0.75 mA, gentle agitation (~15 rpm) was performed during charging, and the charging time was adjusted to control the amount of lithium plating.

*Fabrication of Stretchable Lithium Metal Battery:* The fabrication process for intrinsically stretchable LFP-based cathode, stretchable current collector, and stretchable separator is the same as our previously published paper.[29] For the stretchable collector, a 3:1 weight ratio mixed solution of Ni particles in three different sizes (1:1:1 weight ratio of 325 mesh, 1 μm, and 50 μm), SIBS in cyclohexane, and 10 mg of MWCNT was blade coated onto the glass substrate. The stretchable cathode was prepared by blade coating of functionalized PVDF (F-PVDF) obtained through Fenton reaction, SWCNT and LFP particles mixed in a mass ratio of 2.5:0.5:7 in acetone on the stretchable current collector. After that, the film was dried in a vacuum oven overnight. The SIBS film for the stretchable encapsulant was made by hot-pressing SIBS pellets at 240 °C. Then, the cathode, current collecor, separator, and the Li-GCMMF were sequentially stacked between the SIBS films. The stretchable cell was sealed by 25 wt % SIBS in cyclohexane, and the electrolyte was injected into the cell using a syringe.

*Characterization*: The SEM images were obtained using a field-emission scanning electron microscope (JEOL, JSM-6701F) operated at 5 kV. EDS analysis was also performed using a field-emission scanning electron microscope (ZEISS, Sigma 300), combined with a Bruker XFlash 6I10 detector at acceleration voltage of 5 kV. The process of Li stripping and plating were investigated *via* Li foil/Li-GCMMF symmetric cells (2032-type coin cell) with PP separators. Li foil/Li-

GCMMF symmetric cells were assembled inside an argon-filled glove box (Korea Kiyon Ltd.). The electrolyte used for cell tests was 1 M LiTFSI in DOL:DME (v/v 1:1) with 2 wt% $LiNO_3$. The current density was set to 0.25 $mA \cdot cm^{-2}$ and the charging capacity was set to 0.25 $mAh \cdot cm^{-2}$. Electrochemical impedance spectroscopy was performed at current of 10 mA on a galvanostate in the frequency range of 0.1 Hz to 100 kHz. (Metrohm, Autolab PGSTAT302N & NOVA software 2.1) Battery testing was carried out with a 40-channel battery cycler (WonAtech, WBCS3000S). The stretching tests were performed on a motorized linear stage by subjecting cyclic strains of 40% at a speed of 2 $mm \cdot min^{-1}$. And resistance change during the stretching tests were measured using a Keithley 2000 multimeter.

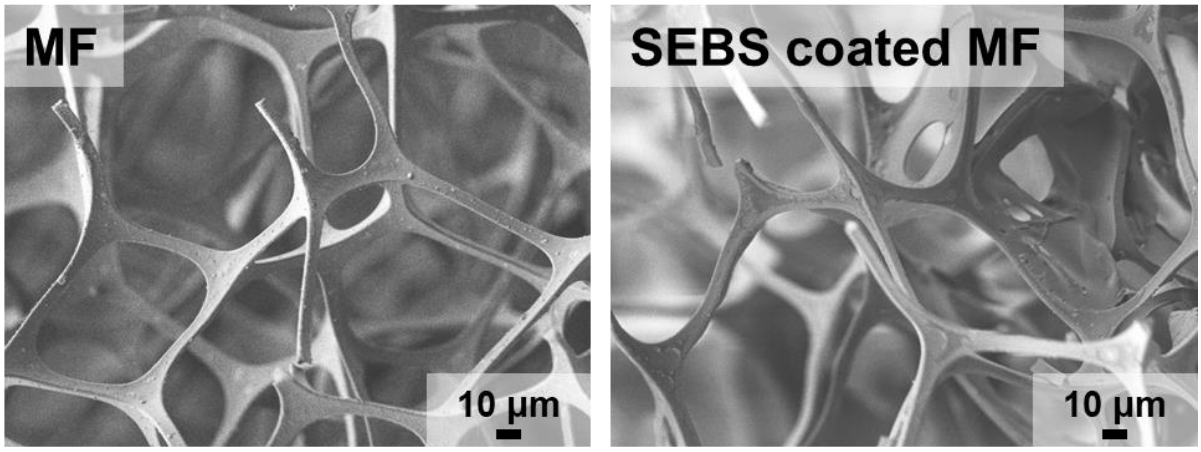


**Figure S1.** SEM images of melamine struts before and after SEBS-coating.

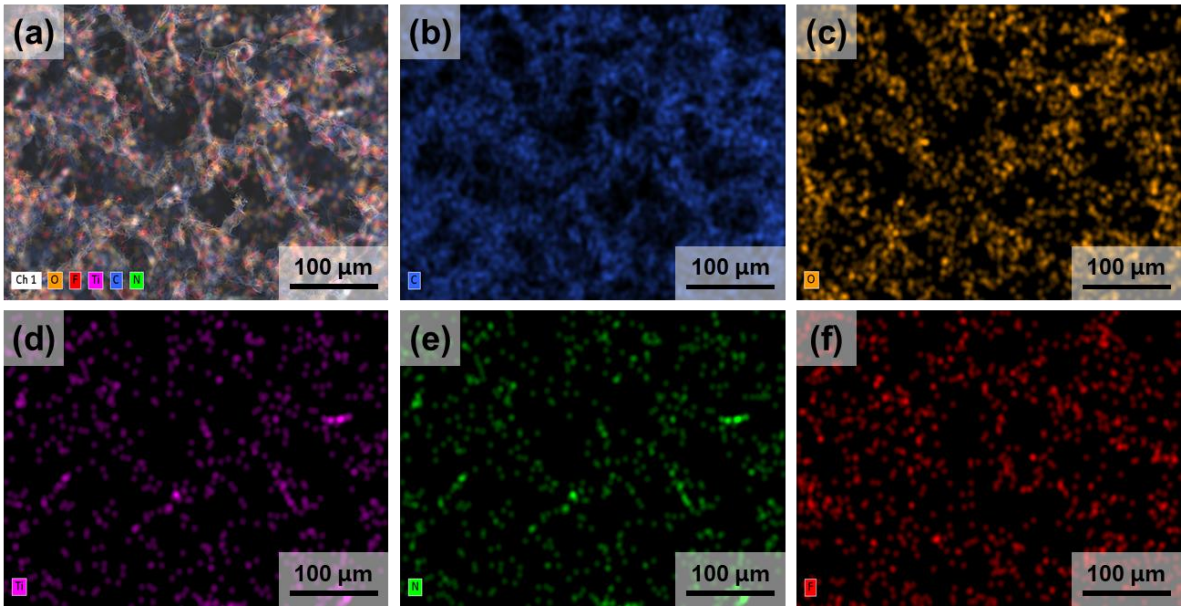


**Figure S2.** EDS elemental mapping of GCMMF: (a) an overlay of C, O, Ti, N, F (b) Carbon (blue), (c) Oxygen (orange), (d) Titanium (Purple), (e) Nitrogen (green), (f) Fluorine (Red).

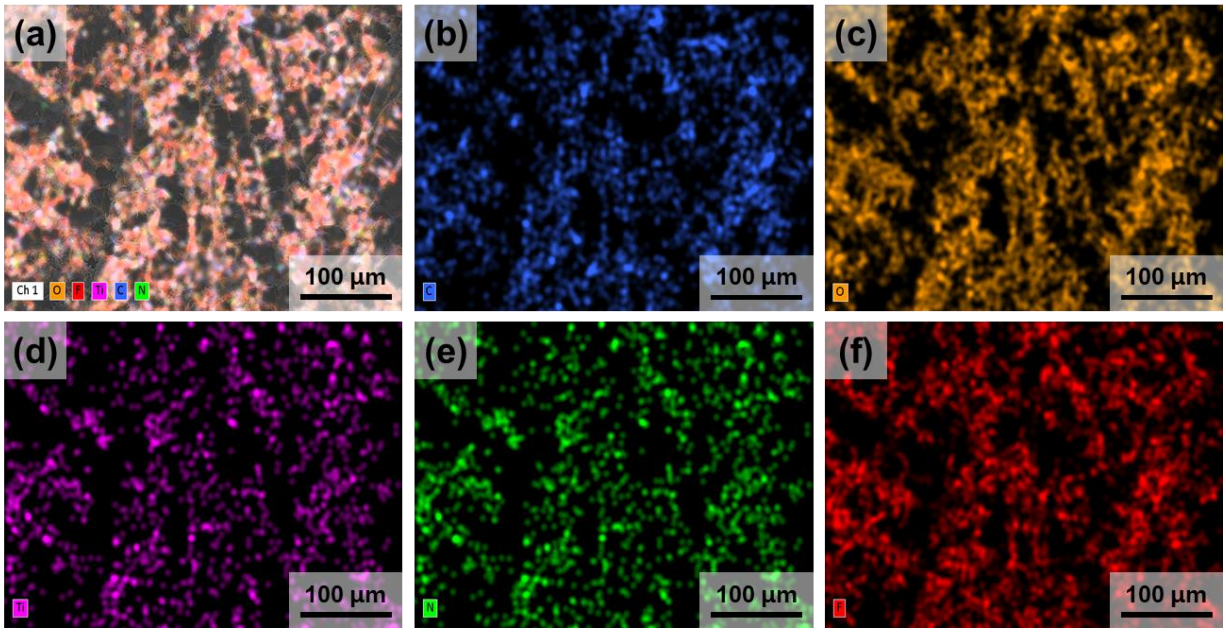


**Figure S3.** EDS elemental mapping of Li-GCMMF: (a) an overlay of C, O, Ti, N, F (b) Carbon (blue), (c) Oxygen (orange), (d) Titanium (Purple), (e) Nitrogen (green), (f) Fluorine (Red).

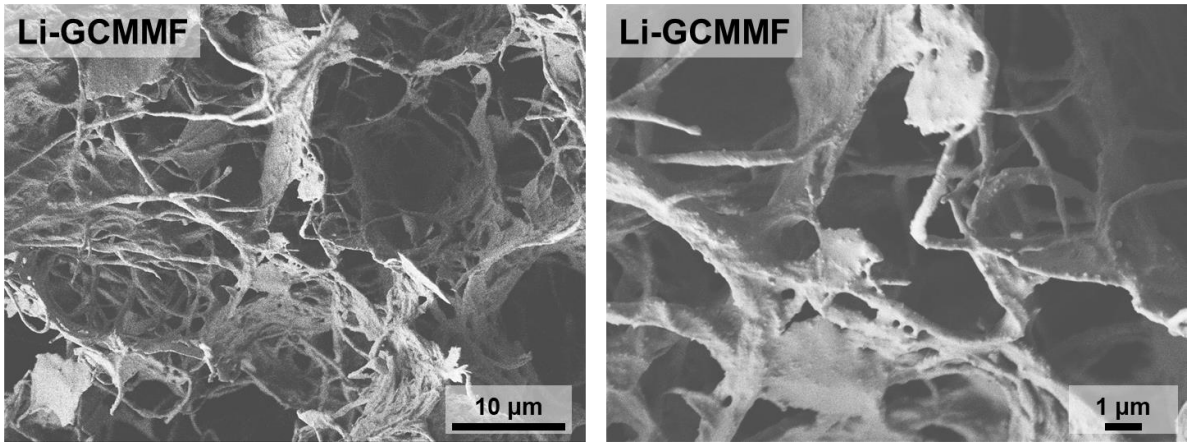


**Figure S4.** High-resolution SEM images of 5 mAh·cm$^{-2}$ deposited Li-GCMMF:

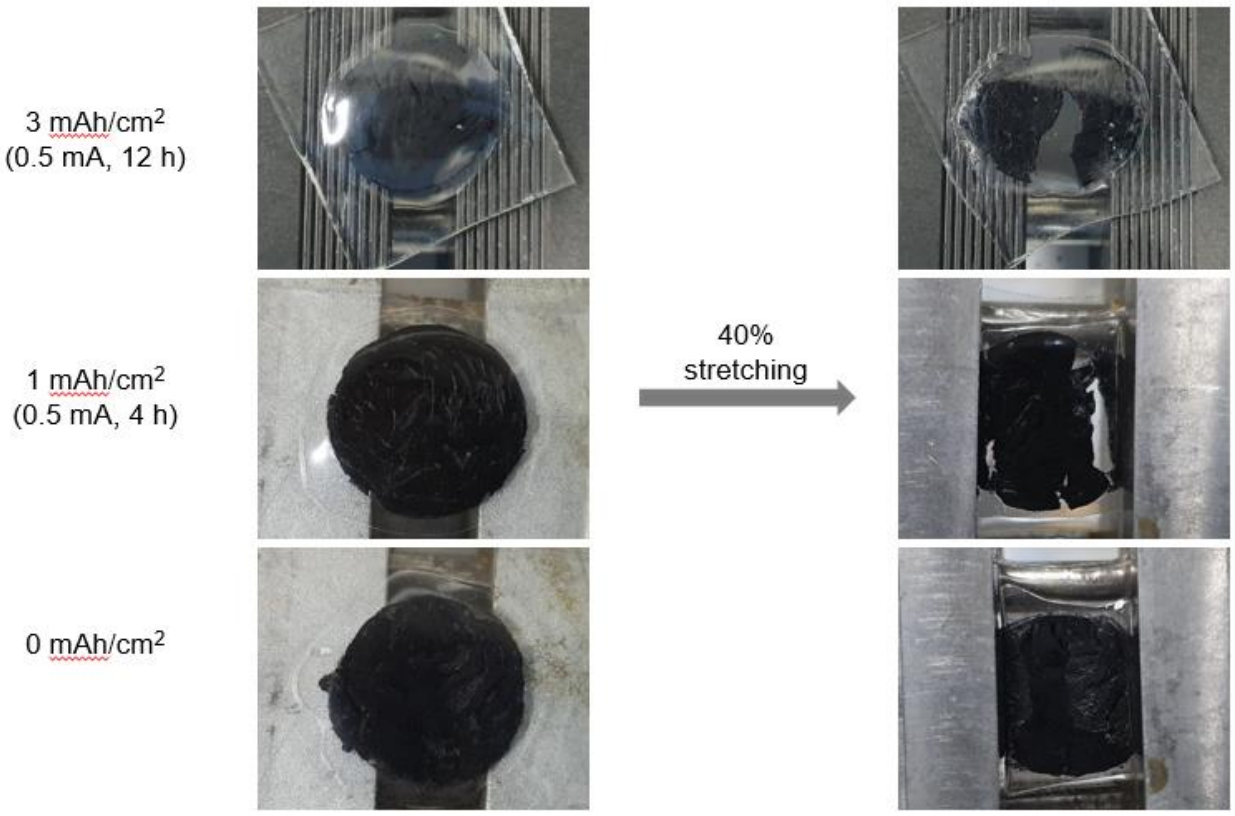


**Figure S5.** Mechanical tension tests of 2D graphene/CNT microcellular frameworks without melamine form with lithium deposition.

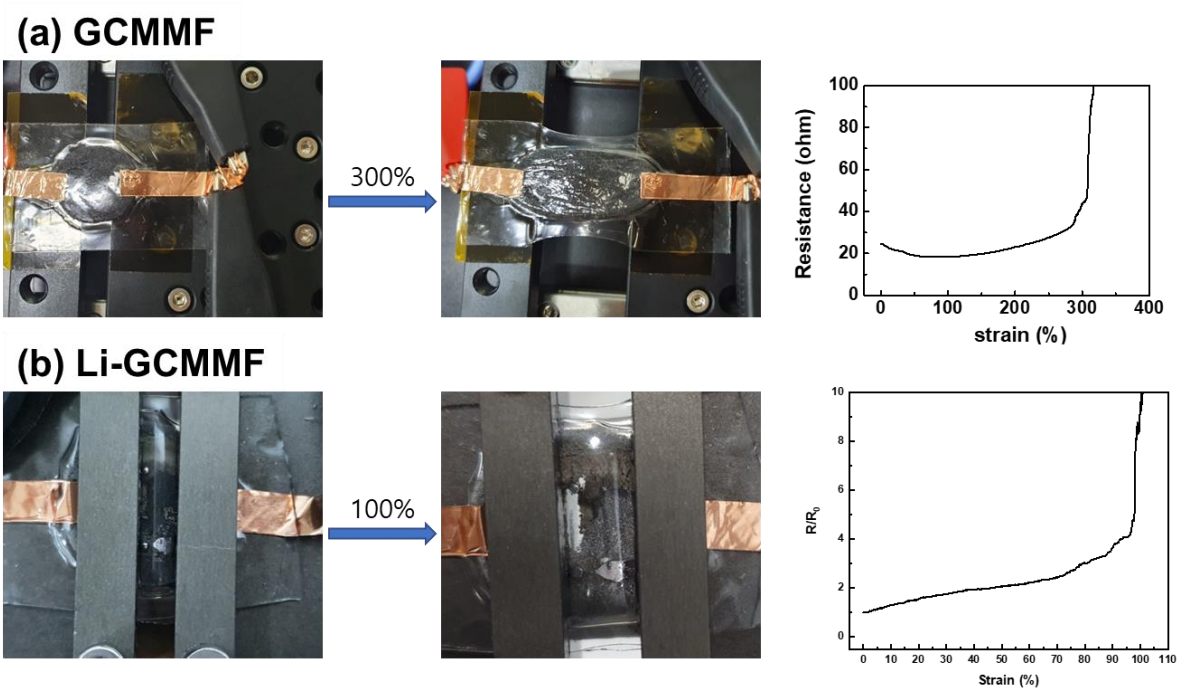


**Figure S6.** Tensile test with resistance changes of (a) GCMMF and (b) Li-GCMMF electrodes.

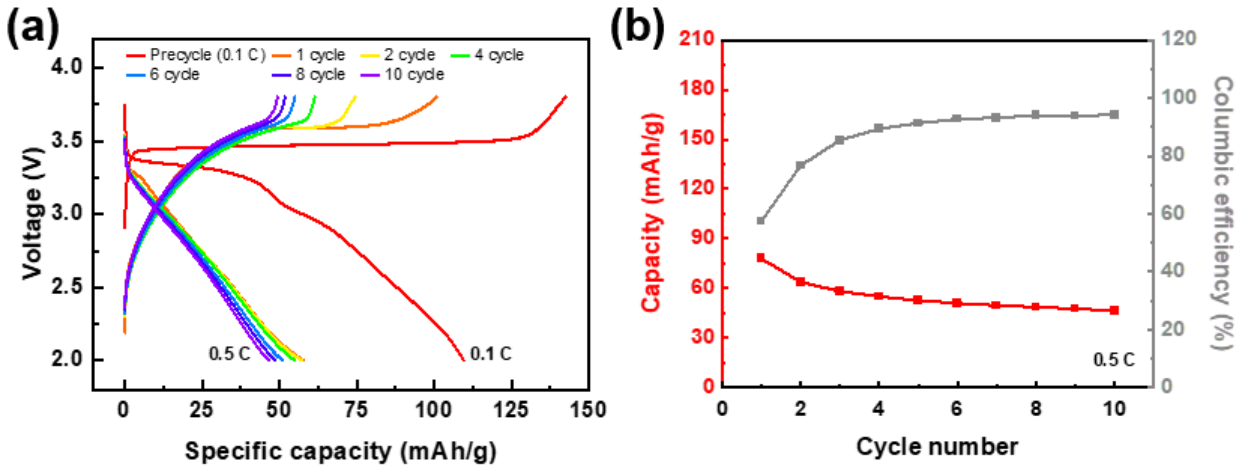


**Figure S7.** (a) Representative charge/discharge curves of Stretchable LMB cell between 2.0 and 3.8 V at 0.5 C, including a precycle of 0.1 C. (b) Coulombic efficiencies of PCOG/LFP half cell at 0.5 C.