Porosity controlled carbon-based 3D anode for lithium metal batteries by a slurry based process

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Experimental

1. Electrode fabrication and characterization

The slurry of the 3D-CPA was prepared by mixing super P black (SPB, 20 wt.%), polyamideimide (PAI, 20 wt.%), and polymethylmethacrylate (PMMA, 15㎛, 60 wt.%) in N-methyl-2-pyrrolidone (NMP). As-prepared slurry was coated on copper foil of thickness 10 ㎛ and dried at 100 ℃ for 4 hours in a forced convention oven. For fabricating the porous electrode, the electrode was heat treated at 400 ℃ for 1 hour under an argon atmosphere to remove PMMA bead completely. Field emission scanning electron microscope (FE-SEM, S-4800; Hitachi) and thermo gravimetric analysis (TGA, SDT Q600, TA instruments) were used to investigate the surface morphology and the fabricating condition of the electrode. The porosity and pore diameter of the 3D-CPA were analyzed using a mercury porosimeter (AutoPore IV 9520, Micromeritics). The Li plated Cu foil and 3D-CPA were characterized by X-ray photoelectron spectroscopy (XPS, ThermoFisher, K-alpha).

2. Electrochemical measurements

Electrochemical tests of Cu foil and 3D-CPA were conducted with CR2032 coin cells, using metallic Li foil as a counter and reference electrode, celgard 2325 as a separator, and 1M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in a mixture of 1,2-dimethoxy ethane(DME)/1,3-dioxolane(DOL)(1:1,v/v) with 1 wt% lithium nitrate ($LiNO_3$) as an electrolyte. The cycling tests of a half cell were performed using Li metal of thickness 500 ㎛ as counter electrode with at the current density of 0.5 mA cm^{-2}. For the full cell test, the cathode slurry consisting of

the active material (80 wt.%, $LiFePO_4$), conductive agent (10 wt.%, Super-P), and binder(10 wt%, PVDF) in an NMP solution, was casted on an Al foil, followed by drying under convention oven at 100 ℃ 12 hours.

LMB full cell was designed and tested by using $LiFePO_4$ (LFP) and 3D-CPA as the cathode and anode, respectively. Before assembling the coin full cell with LFP, 3D-CPA was pre-lithiated electrochemically for 4 mAh-cm^{-2} at current density of 0.1 mA-cm^{-2}. The areal mass loading of the cathode material was 7.0 mg·cm^{-2}. The full cell was galvanostatically cycled at 0.5C between 2.5 V and 4.1 V. The specific capacity was calculated on the basis of the weight of the LFP. The cell was activated at 0.1 C for the first cycle and cycled at 0.5 C for the following cycles. (1 C = 170 mAh·g^{-1}) using a WonA Tech instrument (Standard type WBCS3000S Automatic Battery Charge/Discharge Test System). For measuring the interfacial impedance of the cells, electrochemical impedance spectroscopy (EIS) was conducted with a frequency response analyzer (Biologic, VMP3) at frequencies ranging from 10 mHz to 1 MHz with an amplitude voltage of 5 mV.

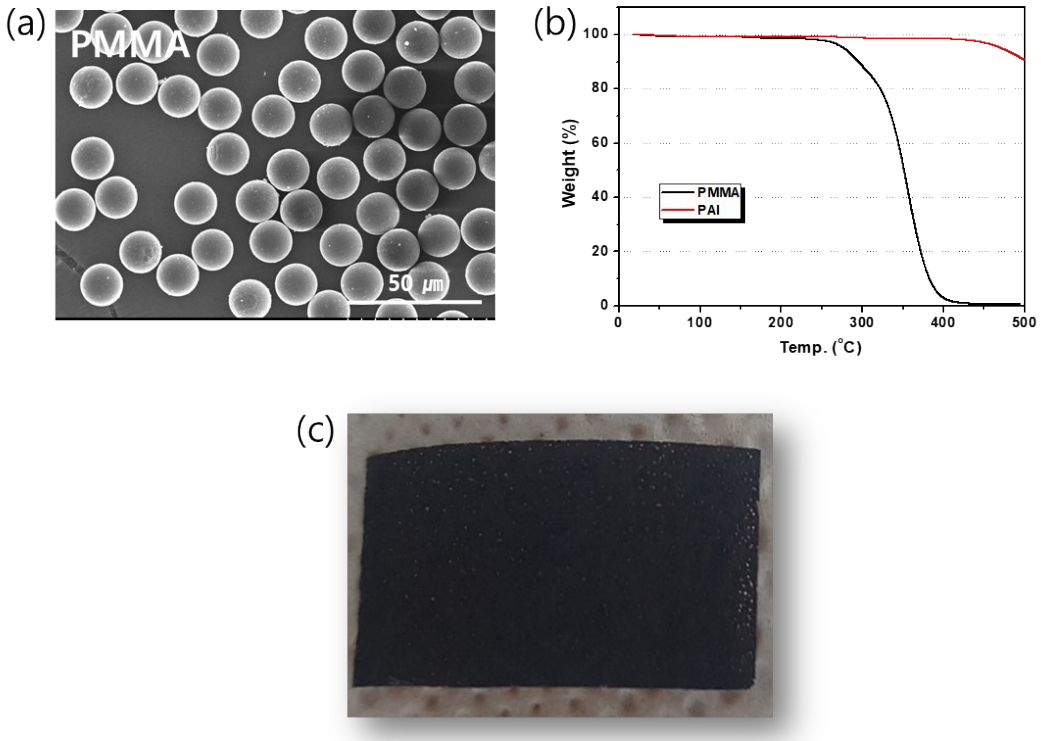

Fig. S1 (a) SEM images of PMMA as pore-forming agent, (b) TGA curve of PMMA and PAI, and (c) optical image of 3D-CPA

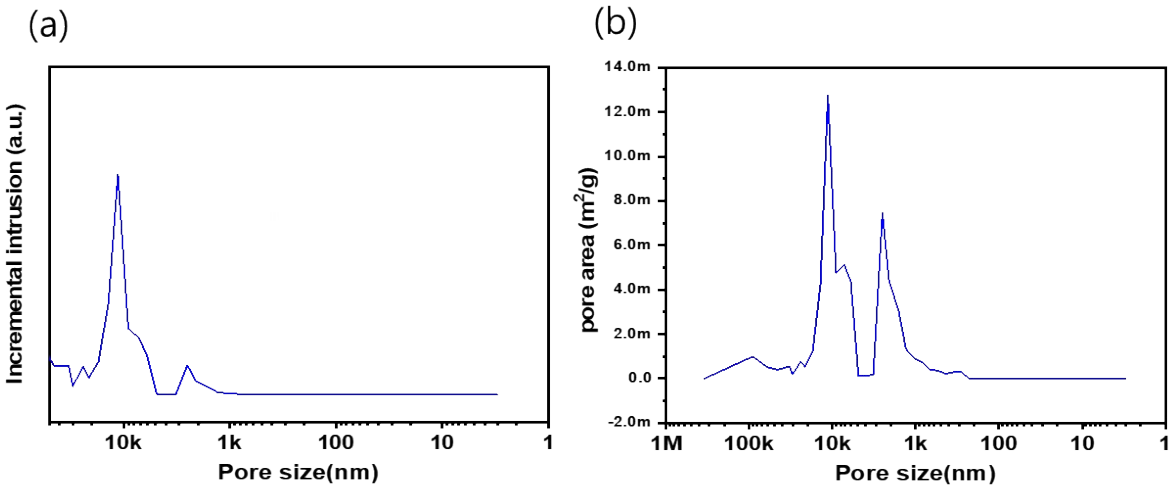

Fig. S2. (a) Pore size distribution and (b) specific pore area of 3D-CPA electrode

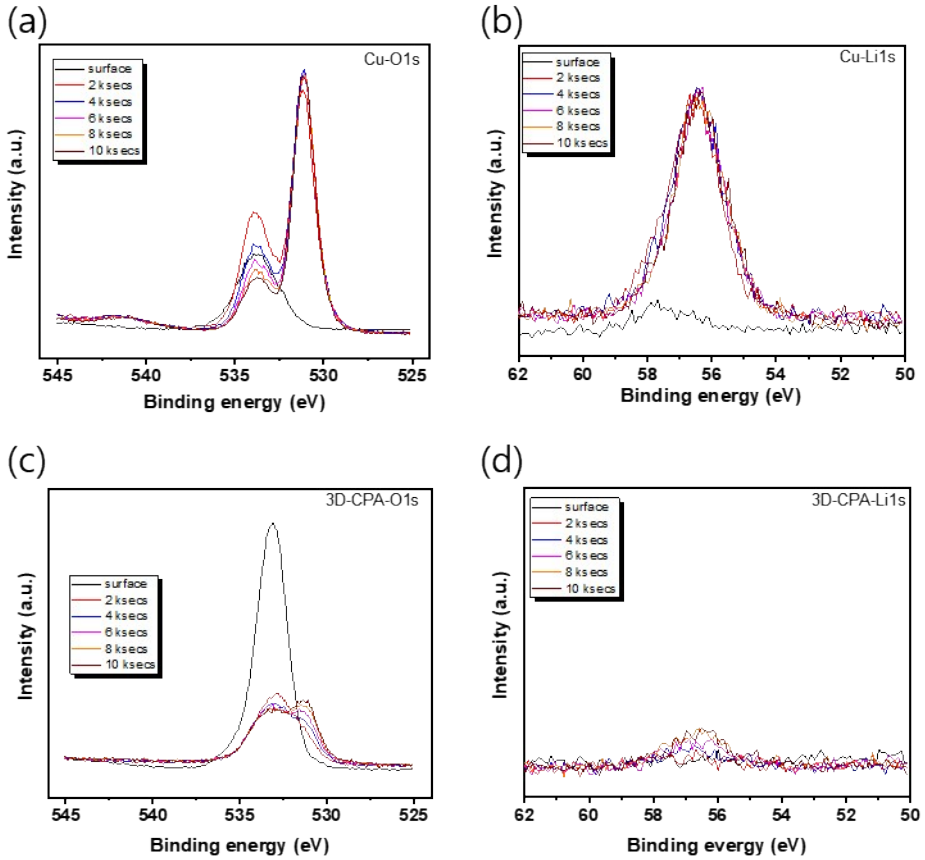

Fig. S3. (a, b) XPS spectrum (O1s, Li1s) of Cu anode, (c, d) 3D-CPA after Li deposition at the first cycle

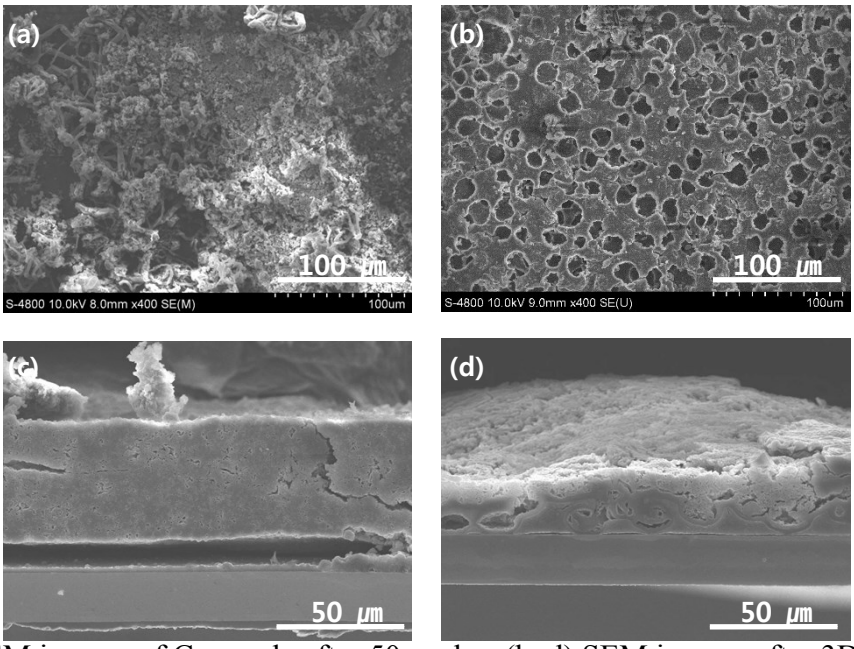

Fig. S4. (a, c) SEM images of Cu anode after 50 cycles, (b, d) SEM images after 3D-CPA after 100 cycles

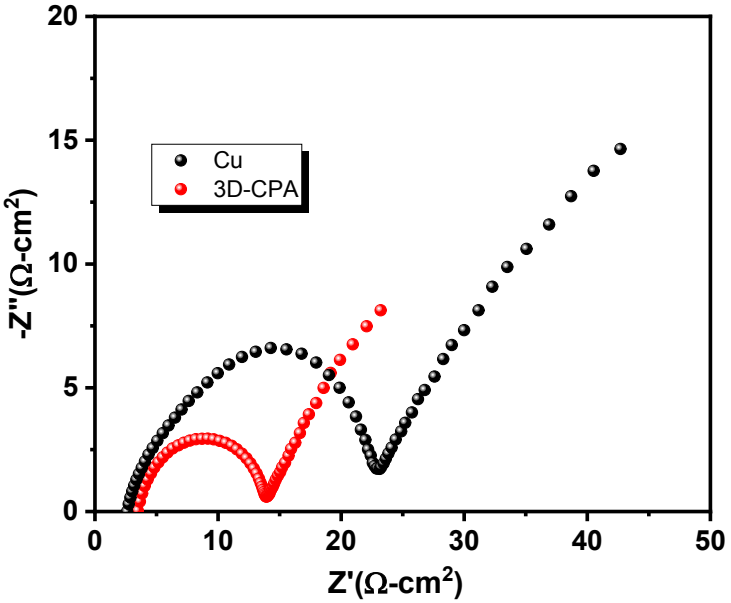

Fig. S5. EIS spectra of Cu and 3D-CPA after 50 cycles

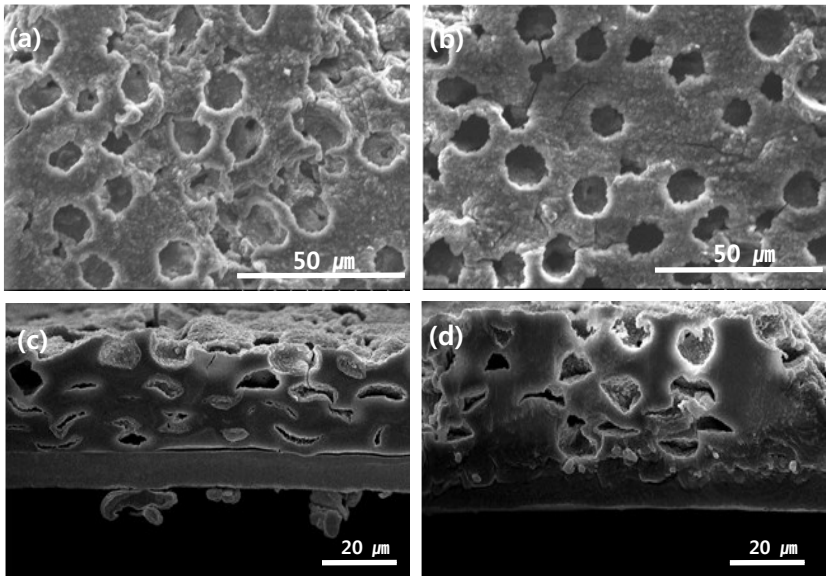

Fig. S6. Top-view and side view SEM images of Li deposition ((a) and (c)) and stripping ((b) and (d)) on 3D-CPA for 4 mAh-cm^{-2} at 0.1 mA-cm^{-2}

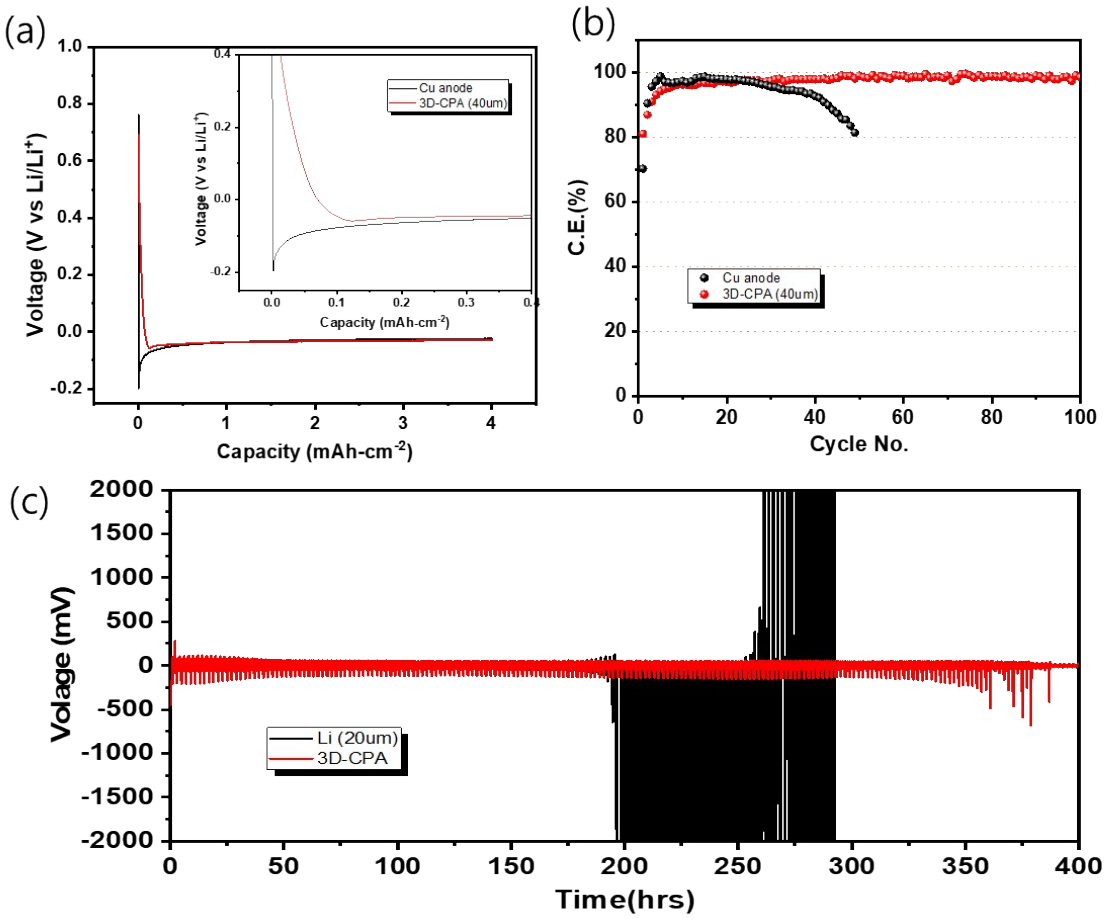

Fig. S7. (a) Voltage profiles for for 4 mAh-cm^{-2} at 0.1 mA-cm^{-2}, (b) cycle performance of Cu anode and 3D- CPA (40 μm) at 0.5 mA-cm^{-2}, and (c) the cycle-ability of symmetry cell test of Li-20 μm and 3D-CPA at current density 1 mA-cm^{-2} with a capacity cutoff of 1 mAh-cm^{-2}

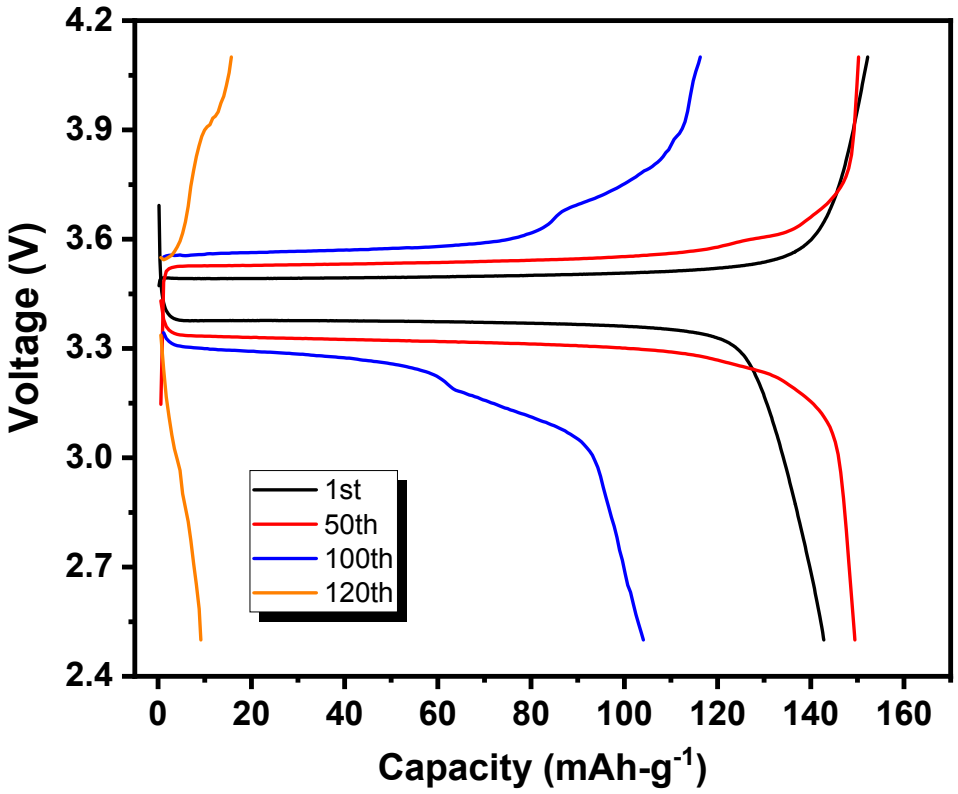

Fig. S8. Voltage profiles of Li-20 ㎛ in the full cell using LFP cathode at 0.5C rate

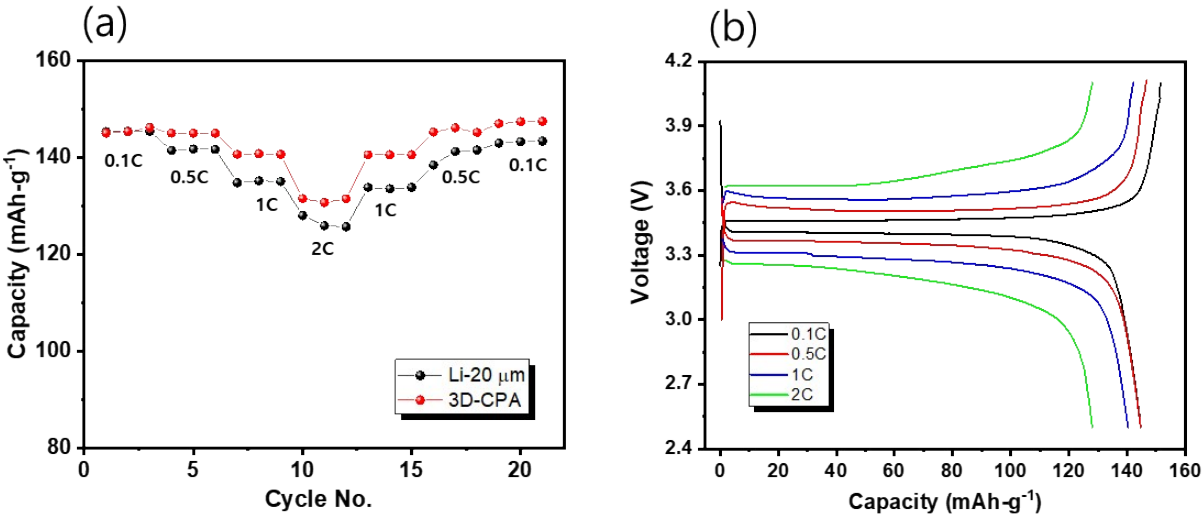

Fig. S9. (a) The reversible capacity at various C-rates for 3D-CPA and Li-20 ㎛ in the full cell using LFP cathode, (b) Voltage profiles of 3D-CPA at various C-rates