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Electronic Supplementary Information

On-site formation of silver decorated carbon as anodeless electrode for high-energy density all-solid-state batteries

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Experimental section

Preparation of anodeless electrodes

Ag nanoparticles (d_{50} = 60 nm, US Research Nanomaterials Inc.), Ag ion complexes, and carbon black (Super C65, Imerys G&C Ltd.) were constituted the materials for the anodeless electrode. The Ag ion complex was a mixture of $AgNO_3$, a chelator, and a thermal reducing agent in IPA. Anodeless electrodes were fabricated by mixing Ag materials, carbon black, and a polyvinylidene fluoride binder in N-methyl pyrrolidinone (Merck) at weight ratios of 25:75:7, 10:90:7, and 5:95:7. N-methyl pyrrolidinone was slowly added to the mixture under constant mixing using a planetary centrifugal mixer (ARE-310, Thinky Corporation) to prepare the anode slurry. The slurry was then coated on 10-μm-thick SUS foil (SUS430D, Nippon Steel), using the doctor blade method, and dried in air at 80 °C for 1 h. The obtained electrode was dried in a vacuum oven at 100 °C for 12 h. The thickness of the anodeless electrodes was 10–20 μm for both electrodes with the carbon-supported silver nanoparticle and particle mixture.

Preparation of cell components

The cathode was prepared by mixing NCM712 ($LiNi_{0.7}Co_{0.1}Mn_{0.2}O_2$, L&F Co. Ltd.), Li_6PS_5Cl (d50 = 1 μm, POSCO JK Solid Solution Co. Ltd.), carbon nanofibers, and PTFE at a mass ratio of 80:18:1:1 for 10 min in a blender. NCM712 was protected by an LZO coating to prevent interfacial side reactions with the solid electrolyte. To fabricate the dry cathode sheet, the prepared powder was mixed and sheared using a heated mortar. The flakes formed by mixing and shearing were rolled to the desired thickness using a roll press. The thickness of the cathode sheet was ~135 μm and the loading level was 6.2 mAh cm^{-2}. A solid electrolyte sheet was prepared using a wet-casting process. A Li6PS5Cl solid electrolyte (d50 = 5 μm) and nitrile butadiene rubber (2 wt. %) in n-butyl butyrate were mixed using the planetary centrifugal mixer (ARE-310, Thinky Corporation) at 2000 rpm for 5 min. The resulting mixture was coated on a release polyethylene terephthalate film using a doctor blade and the film was dried on a hotplate at 40 °C for 2 h and then in the vacuum oven at 60 °C overnight. The thickness of the prepared SSE sheet was ~100 μm, which was further reduced to 80 μm after pressurization in a cell. All processes were performed in a dry room (dewpoint below –50 °C).

Material characterization

To confirm the structure of the anodeless materials, XRD patterns of the samples were obtained using an Empyrean diffractometer (PANalytical) equipped with a monochromatic Cu Kα-radiation source (λ = 1.54 056 Å). Raman spectra were acquired using a Raman spectrometer (DXR3xi, Thermo Fisher Scientific) equipped with a 532 nm laser. XPS (VG Multilab ESCA system, 220i) was used to examine the nature of the reduced silver nanoparticle and carbon black. The chemical structure of the Ag ion complex was determined using Fourier-transform infrared spectroscopy (FTIR, FTIR 670, Varian). The local distribution of the silver nanoparticle on the anodeless electrode was examined using TOF-SIMS (TOF-SIMS 5, ION TOF). The amount of Ag nanoparticles on the electrodes was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES, 700-ES, Varian). The morphologies of the anode and Li deposition were observed using field-emission SEM (FE-SEM, JSM-IT200, JEOL) combined with energy-dispersive X-ray spectroscopy (EDS). SEM samples were prepared using a cross-sectional polisher (SM-09010, JEOL). The cross-sectional images were acquired using focused ion beam (FIB-SEM) technique (Helios Nano Lab 450, FEI) equipped with a Ga-ion milling instrument. Morphological inspection of the anode materials and carbon-supported silver nanoparticles were performed using transmission electron microscopy (TEM; ARM-200F, JEOL) combined with EDS.

Electrochemical characterization

To investigate the electrochemical characteristics of the anodeless electrodes, C/Ag | Li_6PS_5Cl | Li cells were prepared using a polyaryl ether ketone mold. An Li_6PS_5Cl pellet (100 mg, diameter: 13 mm) was prepared at 312 MPa. Anodeless electrodes and Li foil were placed on one side of the pellet and pressed at 437 MPa. After pressurization, 65 MPa of external pressure was applied to the cells. The cathode capacity was assumed to be 7 mAh cm-^{2}, and the final discharge voltage was set to 1.5 V. The cycling test was performed for 1 cycle with a C-rate of 0.05 C. Additionally, to analyze the occurrence of overvoltage according to the current density and capacity during the plating/stripping of the C/Ag anodeless electrode, lithium was charged to the Ag-C electrode, and galvanostatic cycling was performed over time. At this time, plating and stripping with current densities of 0.2 mA cm^{-2}, 0.5 mA cm^{-2}, 0.1 mA cm^{-2}, and 2.0 mA cm^{-2} were performed for 1 h and 50 cycles, respectively, for a total of 200 cycles and 400 h. The 300 mAh-class pouch-type full cell was fabricated to assess cycling and rate capabilities. The electrodes and solid electrolyte sheets were cut using Thompson knives. The dimensions of the anode, cathode, and solid electrolyte were 42 × 62 mm, 40 × 60 mm, and 44 × 64 mm, respectively. All electrodes and electrolyte sheets were stacked and packed into a laminate bag. After applying a vacuum to the laminate bag, it was sealed, and the cell was pressurized at 490 MPa using a WIP (ILSHIN Autoclave). Most of the assembly process, except the isostatic press, were carried out in a dry room (dewpoint below –50 °C). The pouch-type cells were placed between pressure jigs and fastened at a pressure of approximately 4 MPa. The cycle test was performed up to 500 cycles (1 C = 180 mA g^{-1}) with a current density of 0.5 C at 60 °C and 0.2 C at 30 °C, respectively, at 2.5–4.25 V. The rate performance was tested by charging at 0.1 C within the same voltage range and then discharging at 0.1 C, 0.2 C, 0.33 C, 0.5 C, and 1.0 C.

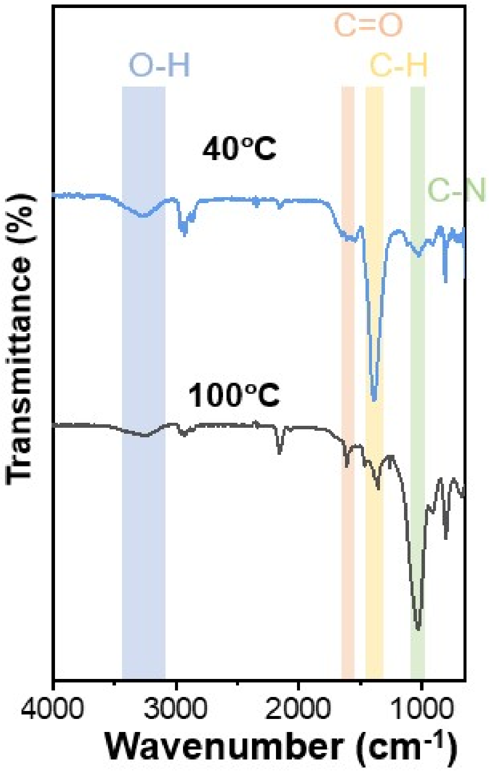

Figure S1. FT-IR spectra of Ag ion complex dried at 40°C and 100°C.

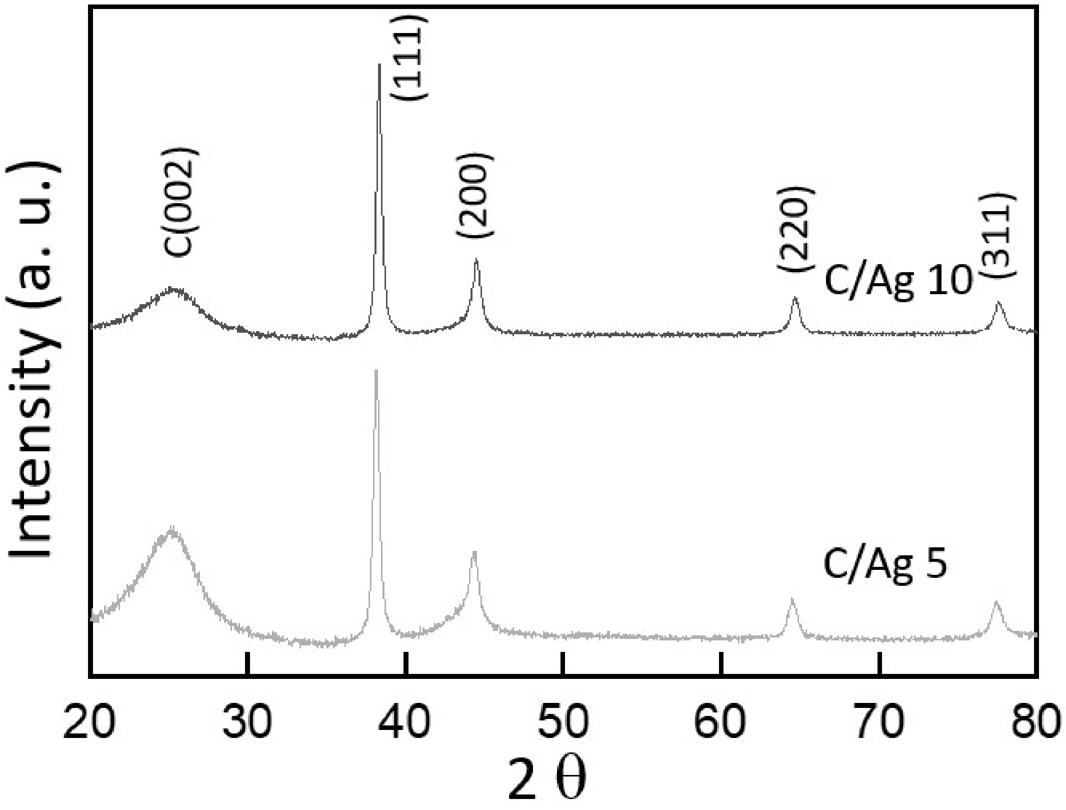

Figure S2. (a) PXRD patterns of C/Ag 10 and C/Ag 5 for carbon supported silver nanoparticles and C-Ag powder mixtures

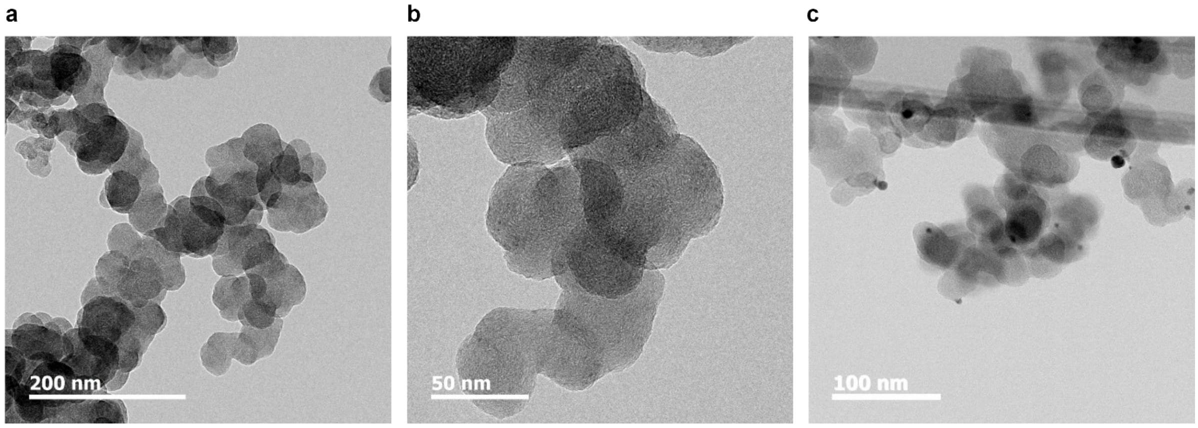

Figure S3. TEM images: carbon black (a-b) and C@Ag-IC 25 (c).

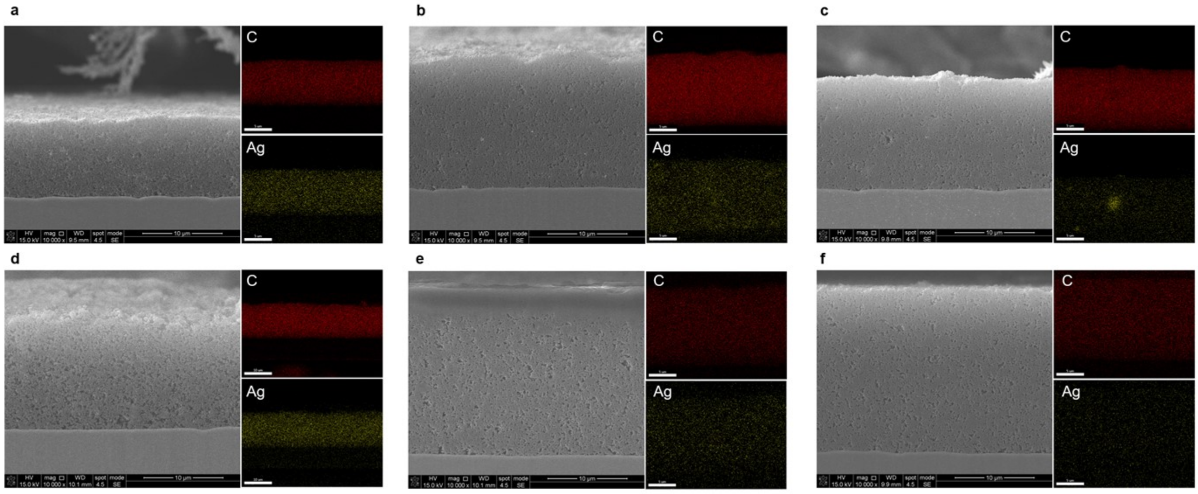

Figure S4. Cross-section SEM image of anodeless electrode: (a) C/Ag 25, (b) C/Ag 10, (c) C/Ag 5, (d) C@Ag-IC 25, (e) C@Ag-IC 15 and (f) C@Ag-IC 5.

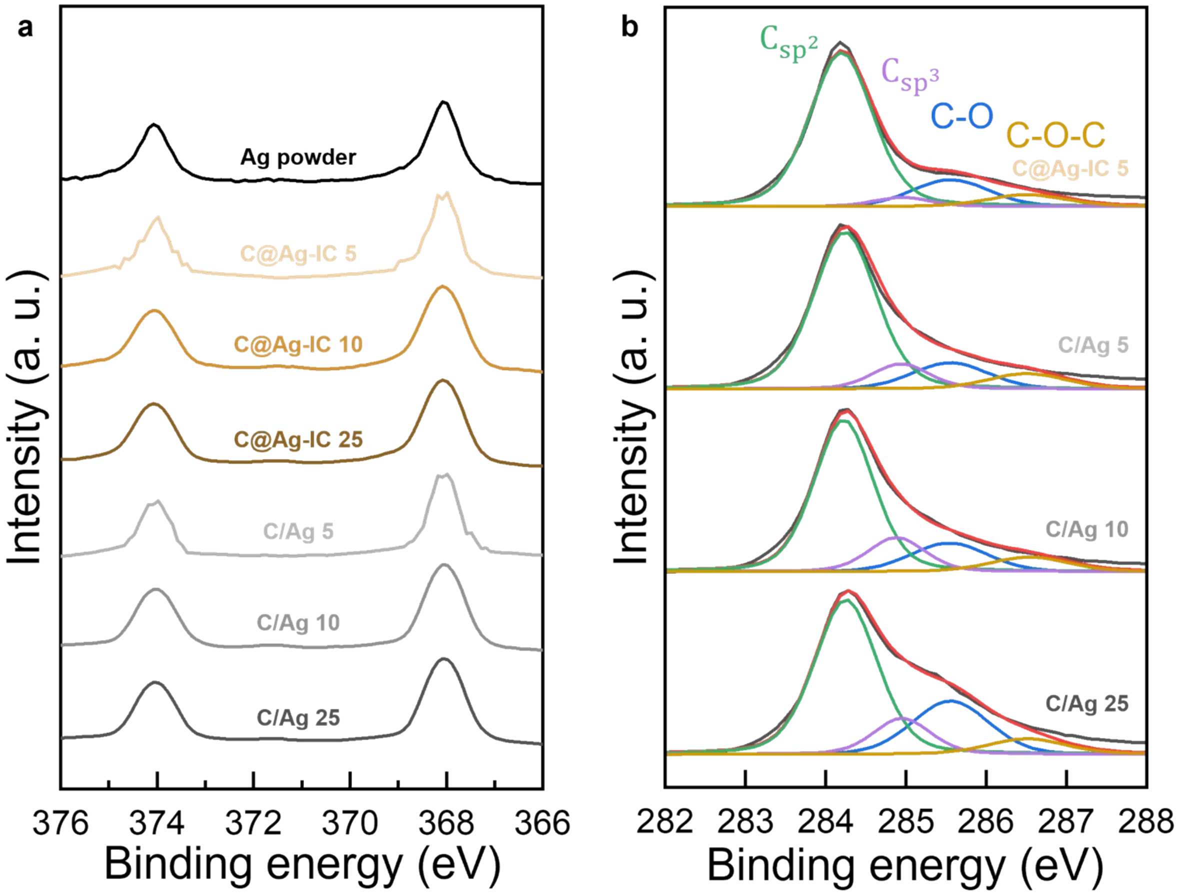

Figure S5. (a) XPS Ag 3d spectra of silver nanoparticle and anodeless electrodes. (b) XPS C1s spectra of C@Ag-IC 5 and C/Ag anodeless electrodes.

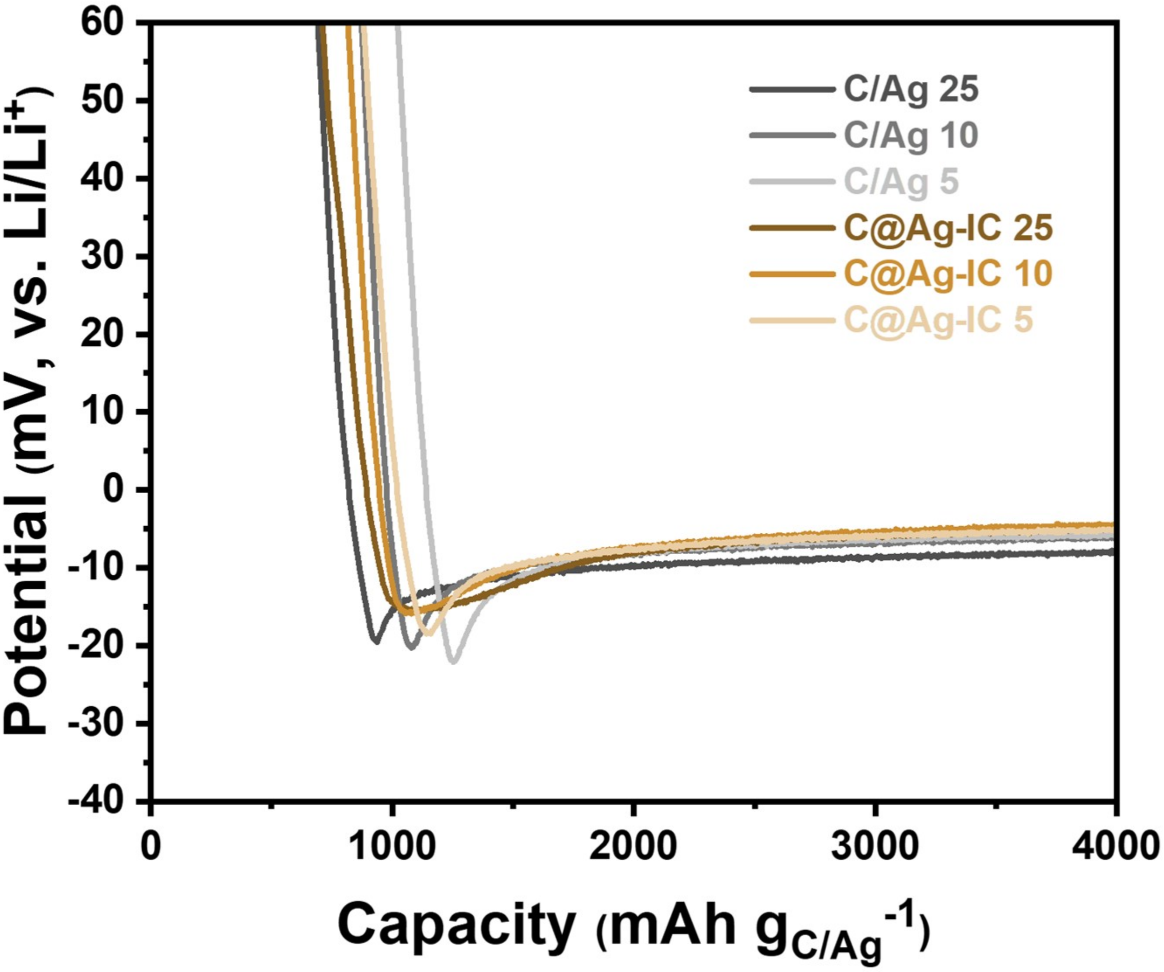

Figure S6. Voltage profiles of anodeless electrodes at initial Li deposition

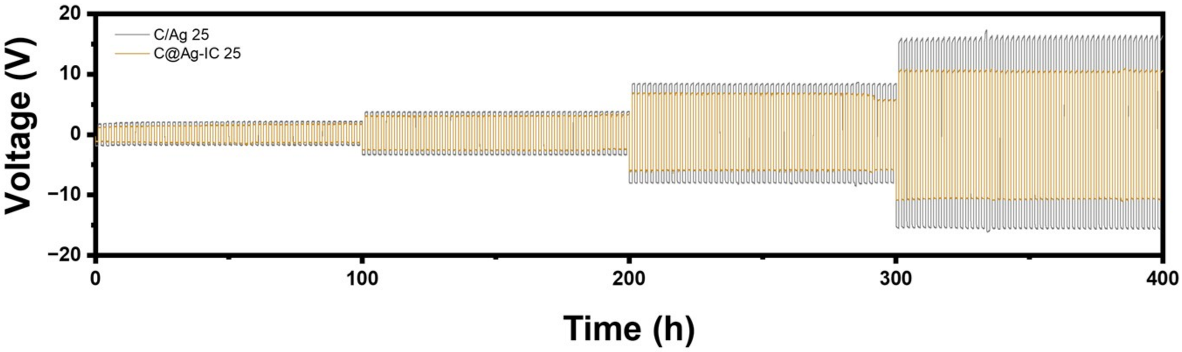

Figure S7. Galvanostatic cycling of anodeless electrodes (C/Ag 25, C@Ag-IC 25) at a current density of 0.2, 0.5, 1, 2 mA cm^{-2}.

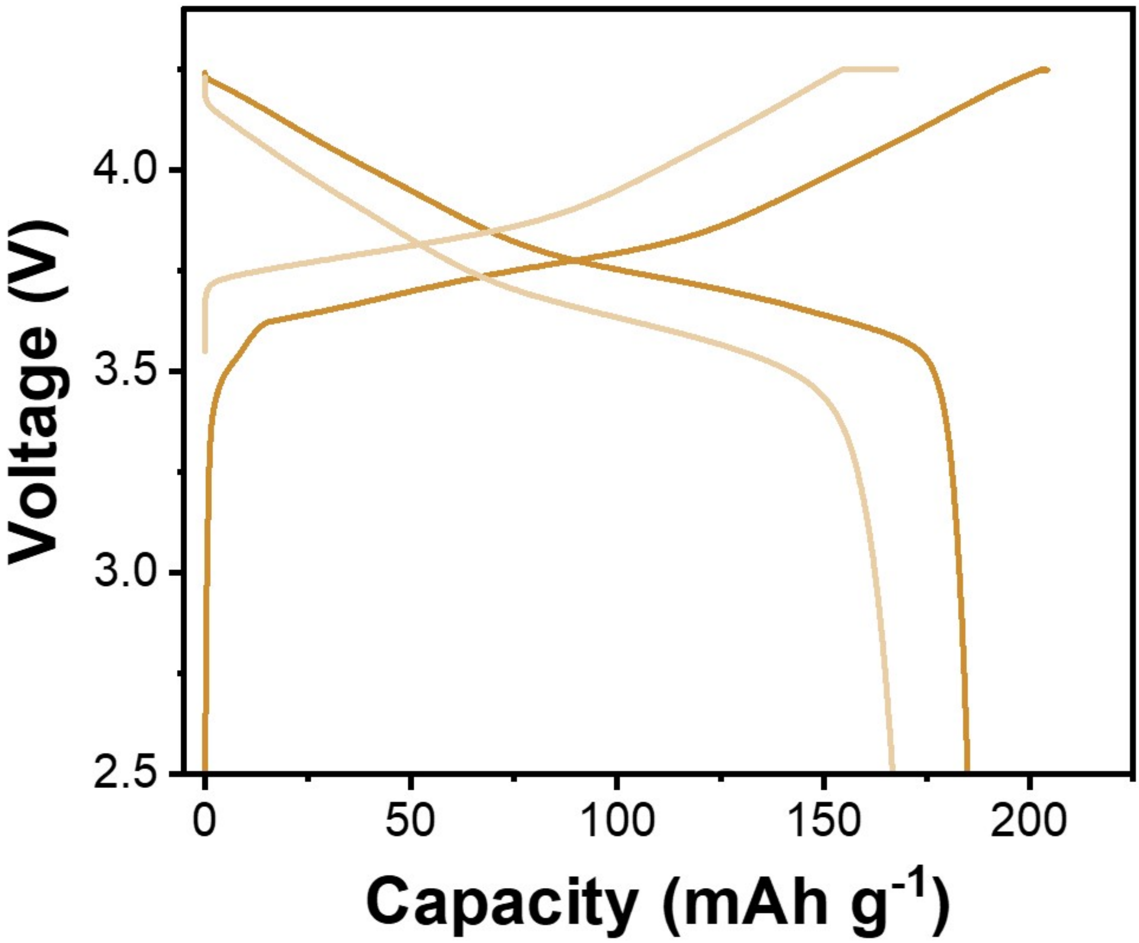

Figure S8. Specific capacity-voltage profiles of full cell ssembled with C@Ag-IC 10 anodeless electrode at a C-rate of 0.1C and 0.5C.

Table S1. ICP measurement data: Ag content in anodeless electrodes

Sample	Ag (wt.%)
C/Ag 25	22.2
C@Ag-IC 1	1.2
C@Ag-IC 5	4.3
C@Ag-IC10	8.6

Table S2. The ratio of the integrated area of deconvoluted peaks of Ag 3d.

Sample	Ag^{2+} (%)	Ag^{+} (%)	Ag^{0} (%)
C@Ag-IC 1	19.46	36.67	43.87
C@Ag-IC 5	1.30	8.51	90.19
C@Ag-IC 10	0.63	6.14	93.23
C@Ag-IC 25	0.60	5.82	93.58