

**Sulfur Covalently Bonded to Porous Graphitic Carbon as an Anode Material for Lithium-Ion  
Capacitors with High Energy Storage Performance**

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## METHODS

**Materials.** All chemicals (analytical grade reagents) were purchased from Aladdin Reagent (Shanghai) Co., Ltd. and used without further treatment.

**Synthesis of CB-S@PGC.** Starch (0.8 g) was added into DI water (50 mL), followed by stirring at 110 °C to obtain a transparent solution. Then the starch solution was cooled down to room temperature. NaCl (5.0 g) and Na<sub>2</sub>S·9H<sub>2</sub>O (2.0 g) were dissolved in DI water (30 mL), followed by addition of the NaCl-Na<sub>2</sub>S solution into the starch solution under magnetic stirring at room temperature. The water was removed from the solution by freeze-drying and the resulting composite was designated as NaCl-Na<sub>2</sub>S@starch. And then, the NaCl-Na<sub>2</sub>S@starch was thermally treated at 750 °C for 2 h under an atmosphere of Ar, leading to carbonization of the starch. The obtained product was designated as NaCl-Na<sub>2</sub>S@GC. The NaCl-Na<sub>2</sub>S@GC was added in to a solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (20 g) in DI water (150 mL) and the suspension was stirred for 39 h, leading to the formation of macropores upon dissolution of the NaCl crystals and the *in situ* formation of sulfur nanoparticles in the PGC due to the oxidation of Na<sub>2</sub>S by Fe(NO<sub>3</sub>)<sub>3</sub>. The obtained S@PGC was dispersed in CS<sub>2</sub> (30 mL), followed by keeping standing for 8 h, to remove free sulfur. PGC was prepared following the above process, but without the use of Na<sub>2</sub>S·9H<sub>2</sub>O in the preparation. An S/PGC mixture that had the same S content as CB-S@PGC was prepared by a thermal infiltration process carried out at 155 °C for 12 h.

**Materials Characterization.** TGA measurements were carried out with a TGA Q50. FT-IR spectra were collected on an Excalibur 3100 spectrometer. Raman spectra were collected on a Renishaw inVia-Reflex confocal Raman microscope. Carbon K-edge XANES measurements were

performed in an ultrahigh vacuum chamber ( $10^{-5}$ – $10^{-6}$  Torr) at the soft X-ray spectroscopy beamline (BL08U1-A) of Shanghai Synchrotron Radiation Facility (SSRF). XPS spectra were collected on a PHI Quantera Scanning X-ray Microprobe.  $N_2$  adsorption–desorption isotherms and pore-size distribution were obtained at 77 K using ASAP2460 apparatus. XRD patterns were collected on a Bruker D8 Focus diffractometer using an incident wavelength of 0.154 nm (Cu  $K\alpha$  radiation) and a Lynx-Eye detector. The morphology of the samples was studied by field-emission SEM (Hitachi S-4800) and by TEM (Hitachi HT7700).

**Electrochemical measurements and analyses.** CR2032 coin LIC cells were prepared using the CB-S@PGC composite as anode, activated carbon (AC) as cathode, a solution of lithium bis(trifluoromethane)sulphonimide (LiTFSI, 1.0 M) in the mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DOE) (1:1 v/v) as electrolyte, and a porous membrane (Celgard 2325) as separator in an Ar-filled glove box. Anodes were prepared as follows: The CB-S@PGC composite (70 wt%) were combined with acetylene black (15 wt%) as electric conductor and poly(vinylidene fluoride) (PVDF) (15 wt%) as a binder in *N*-methylpyrrolidone (NMP), and milled into a slurry. The slurry was blade cast onto stainless steel grids and dried under vacuum at 50 °C for 3 h. The quantity of CB-S@PGC on each stainless steel grid was approximately 1.5 mg. As a control, S/PGC composite that was prepared by thermal impregnation of sulfur into PGC (*i.e.*, 155 °C for 12 h) was used to prepare anodes following the same procedure. Cathodes were prepared as follows: AC (80 wt%) was combined with acetylene black (10 wt%) and PVDF (10 wt%) as binder in NMP, and milled into a slurry. The

slurry was blade cast onto stainless steel grids and dried under vacuum at 50 °C for 3 h. The quantity of AC coated on each stainless steel grid was 9–10 mg.

LiCoO<sub>2</sub> electrodes that have more positive potential were also used as cathode to measure the electrochemical performance of CB-S@PGC electrode. A solution of LiTFSI (1.0 M) in the mixture of DOL and DOE (1:1 v/v) was used as electrolyte. To independently measure the the potential of LiCoO<sub>2</sub> electrodes, CR2032 coin cells were prepared using LiCoO<sub>2</sub> as cathode and Li foil as anode.

Li–S half cells (CR2032 coin cells) were prepared using the CB-S@PGC composite as cathode, lithium foil as anode, and a solution of LiTFSI (1.0 M) in the mixture of DOL and DOE (1:1 v/v) as electrolyte.

Symmetric supercapacitors were prepared using pristine PGC or CB-S@PGC as electroactive materials. The electrodes were prepared by as follows: PGC or CB-S@PGC composite (70 wt%) was combined with acetylene black (25 wt%) and polytetrafluoroethylene (5 wt%) in ethanol, and milled until the ethanol evaporated. The mixture was pressed into films and then cut into discs as supercapacitor electrodes. A symmetric supercapacitor was prepared by assembling two discs, that was separated by a porous membrane (Celgard 2325), between a pair of stainless steel plates as current collectors using 3 M KOH solution as electrolyte.

Cyclic voltammetry curves and galvanostatic charge/discharge curves were collected using a CHI 660E electrochemical workstation. The specific capacitance ( $C$ , F g<sup>-1</sup>), energy density ( $E$ , Wh kg<sup>-1</sup>), and power density ( $P$ , W kg<sup>-1</sup>) were calculated from the galvanostatic charge/discharge curves using the following equations:

$$C = \frac{2I(t_2 - t_1)}{mV} \quad (3)$$

$$E = \int_{t_1}^{t_2} IV dt \quad (4)$$

$$P = \frac{E}{t_2 - t_1} \quad (5)$$

where  $I$  is the current density ( $\text{A kg}^{-1}$ ) used in galvanostatic charge/discharge tests,  $m$  is the mass (g) of electroactive materials.  $V$  is the voltage (V) applied to the two current collectors, and  $t_1$ ,  $t_2$  are the starting and ending time for a discharge process, respectively. These parameters for the LIC cells were normalized on the basis of the mass of the CB-S@PGC composite.

Cycling tests of the devices were galvanostatically performed at  $4 \text{ A g}^{-1}$  on a Landian battery measurement system.

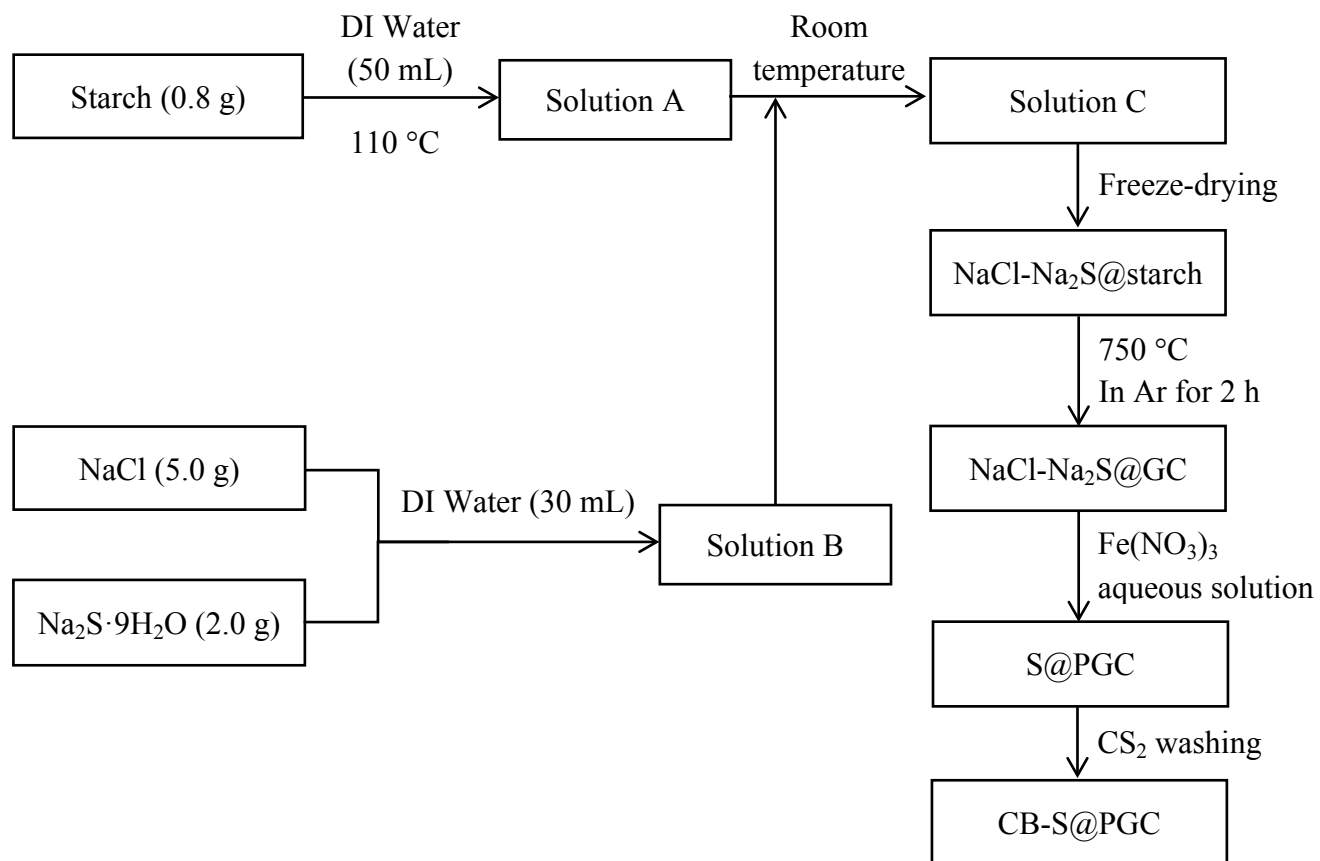


Fig. S1. The synthetic route for CB-S@PGC composite.

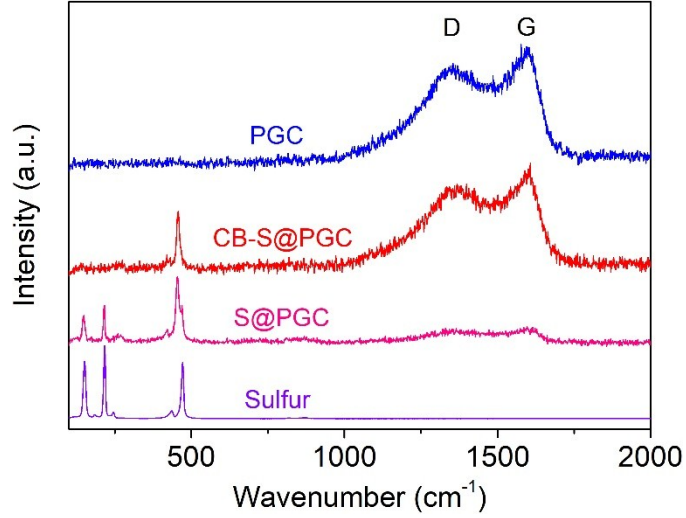


Fig. S2. Raman spectra of sulfur, S@PGC, CB-S@PGC, and PGC.

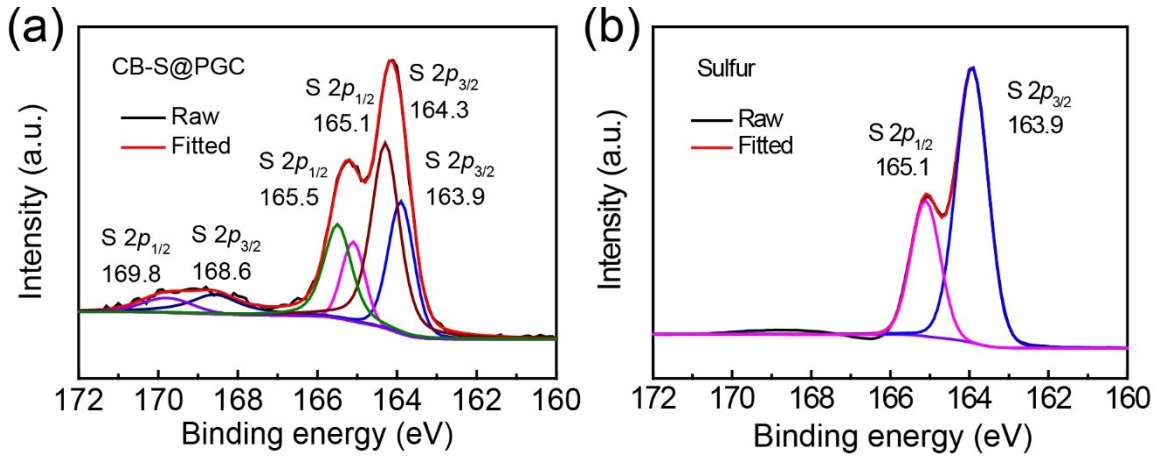


Fig. S3. S 2p XPS spectra of (a) CB-S@PGC composite and (b) sulfur. By fixing the S  $2p_{3/2}$  and S  $2p_{1/2}$  signals of pure sulfur at 163.9 and 165.1 eV, two more signals can be obtained at 164.3 and 165.5 eV, reconfirming the presence of C–S bonds in CB-S@PGC. The peaks at 168.6 and 169.8 eV can be ascribed to the S  $2p_{3/2}$  and S  $2p_{1/2}$  signals of sulfate due to the oxidation of sulfur.

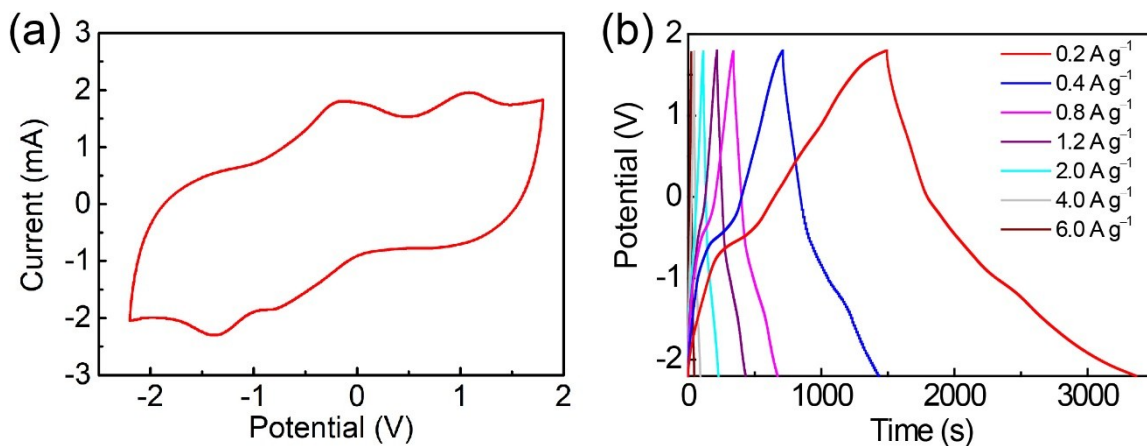


Fig. S4. Electrochemical characterization of PGC electrode using AC as counter electrode. (a) CV curves. (b) Galvanostatic charge/discharge curves.

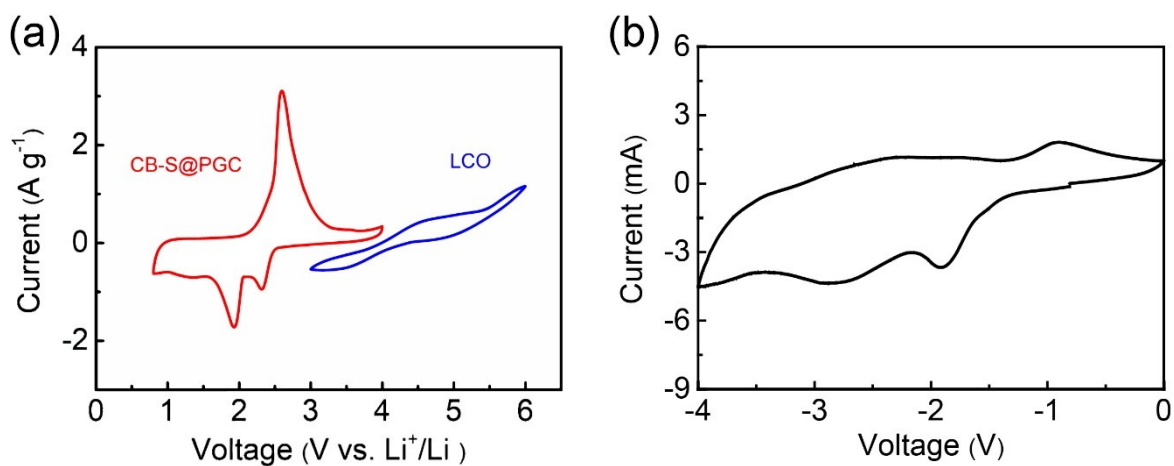


Fig. S5. (a) The CV curves of CB-S@PGC electrode and LCO electrode recorded at a scan rate of 2 mV s<sup>-1</sup> using Li foil as counter electrode. (b) The CV curve of a CB-S@PGC//LCO cell recorded at a scan rate of 2 mV s<sup>-1</sup>.



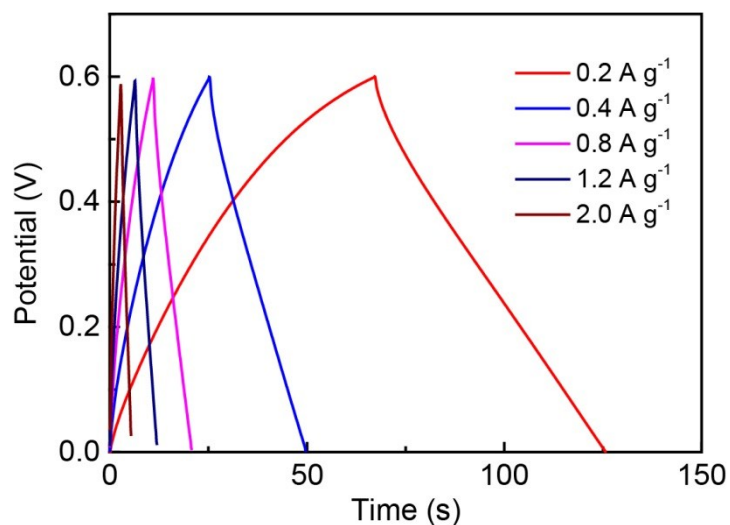


Fig. S6. Galvanostatic charge/discharge curves recorded for a symmetric supercapacitor fabricated using PGC as electrode material. Specific capacitance was measured to be 39.0, 32.7, 26.1, 22.0 and 17.3 F g<sup>-1</sup> at current density of 0.2, 0.4, 0.8, 1.2 and 2.0 A g<sup>-1</sup>, respectively.

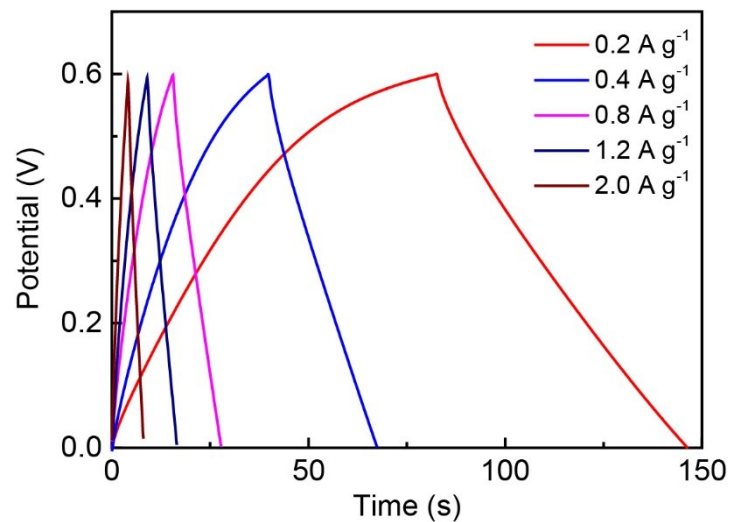


Fig. S7. Galvanostatic charge/discharge curves recorded for a symmetric supercapacitor fabricated using CB-S@PGC composite as electrode material. Specific capacitance was measured to be 42.5, 36.8, 32.5, 30.0, and 26.0 F g<sup>-1</sup> at current density of 0.2, 0.4, 0.8, 1.2 and 2.0 A g<sup>-1</sup>, respectively.

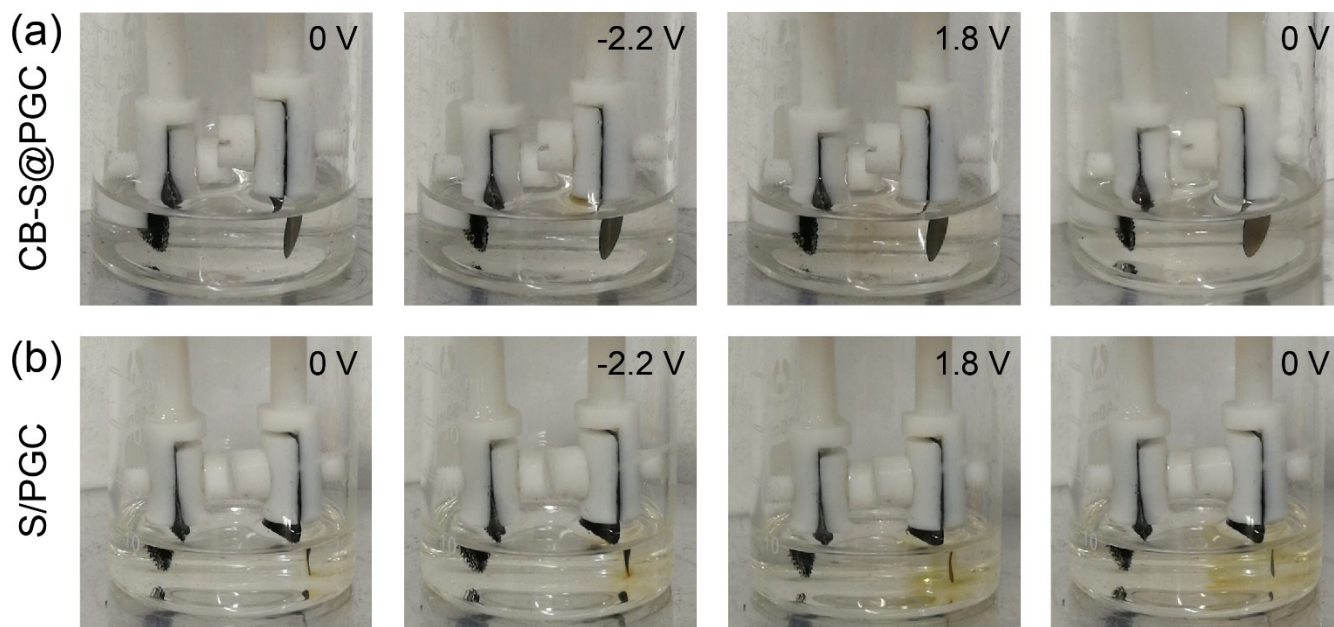


Fig. S8. Photos of the electrolyte containing (a) CB-S@PGC electrode and (b) S/PGC electrode recorded at different potentials with respect to AC during the first charging/discharging cycle.

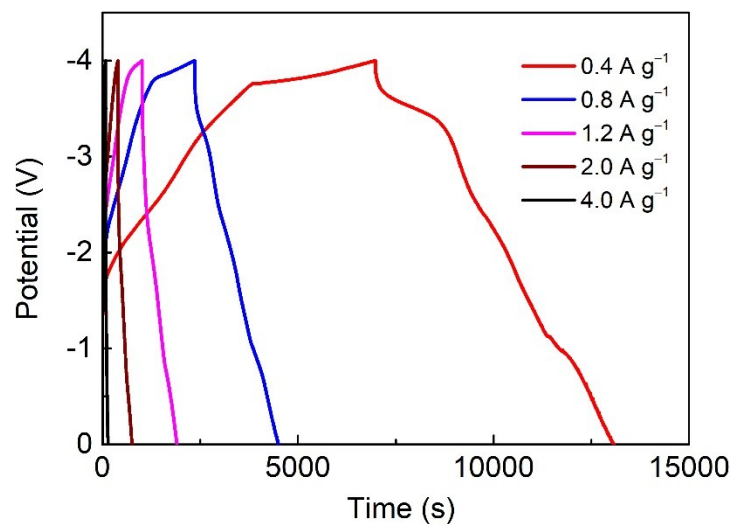


Fig. S9. Galvanostatic charge/discharge curves recorded at various current densities for a CB-S@PGC//LCO cell.