

Supporting information

A Low-Charge-Overpotential Lithium-CO₂ Cell Based on Binary Molten Salt Electrolyte

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Keywords: Li-CO₂ battery, molten salt, cycle stability, inorganic electrolyte, Ru catalyst

Materials preparation. All the containers and salts were dried in vacuum at 110 °C for 24 h, the salts were obtained from Sigma and used as received. Ru@Super P material was synthesized via a very similar method to previous work: 50 mg of RuCl₃·xH₂O (40% Ru content) was dissolved in 100 mL of ethylene glycol. 80 mg of Super P carbon was added into the solution and was uniformly mixed through an ultrasonic bath. The suspension was refluxed for 3 h at 170 °C. After cooling down, the supernatant was removed and the remnant mixture was centrifuged with deionized water and ethanol several times. The resulting products were dried in a vacuum oven at 80 °C for 12 h.

Electrolyte. The molten nitrate salt electrolyte was composed of lithium nitrate (99.99 %, Sigma-Aldrich) and potassium nitrate (≥99.0%, ReagentPlus®, Sigma-Aldrich)

with a mole ratio of 42:58. The organic electrolyte was composed of 1 M Lithium bis(trifluoromethane)sulfonamide (LiTFSI) in TEGDME. Before the preparation of molten nitrate electrolyte, LiNO_3 and KNO_3 were milled together (mole ratio of 42:58) by homogeneous mixing in an Ar-filled glovebox with O_2 and H_2O levels maintained below 0.1 ppm.

Cathode. The CO_2 cathode was prepared by pressing an as-prepared carbon material on the aluminum mesh with a diameter of 12 mm, the carbon material was a mixture of Super P (90 wt%) and polytetrafluoroethylene (PTFE, 10 wt%), no additional conductive additives were applied. The carbon loading on this CO_2 cathode was ~ 2 mg/cm^2 . For molten salt-based Li- CO_2 cell, the as-prepared molten salt electrolyte was heated at 200 °C for 24 h, then, the prepared Super P cathode was impregnated in the molten nitrate.

Assembling cells. The as-prepared electrolyte was heated at 200 °C for 24 h, then, glass microfiber separator (Whatman) was impregnated in the molten nitrate for 5 minutes, the mass of the impregnated separator was increased 140-160 mg. Finally, the Super P cathode (or Ru@Super P cathode), separator, and Li anode were assembled in the homemade cell in a CO_2 -filled homemade mold, the molten salt-cells were operated at 140 °C and the organic electrolyte-cells were operated at room temperature.

Raman analysis. Raman spectra were recorded using the 633 nm line of a semiconductor laser (Raman Confocal SNOM instrument) to investigate the surface composition of electrode, in order to avoid the exposure of the electrode to air, cathodes were removed from the cells and put into a homemade air-tight holder for the

characterization.

GC-MS analysis. In situ gas chromatography-mass spectrometry (GC-MS) measurements were conducted using a homemade cell which was connected to the equipment (Clarus 680 and SQ 8S).

SEM analysis. The Hitachi SU-8010 scanning electron microscope was used to observe the morphology of electrode.

XPS analysis. X-ray photoelectron spectroscopy (XPS) spectra of the electrode were recorded using a Thermo Fisher Scientific Model K-Alpha spectrometer equipped with Al K α radiation (1486.6 eV).

XRD analysis. The structure of the materials prepared in this article is characterized by X-ray diffraction (XRD) (D8 Advance, Bruker).

TG-DTA analysis. Thermogravimetric analysis was conducted on a TA Instrument SDT Q600 at a heating rate of 5 °C·min⁻¹. Ru@Super P was test in air atmosphere at temperature range: 25 ~ 800 °C, and Li₂CO₃-KNO₃-LiNO₃ was test in Ar atmosphere at temperature range: 30 ~ 300°C.

FTIR analysis. The ATR-FTIR spectra were obtained from NEXUS870.

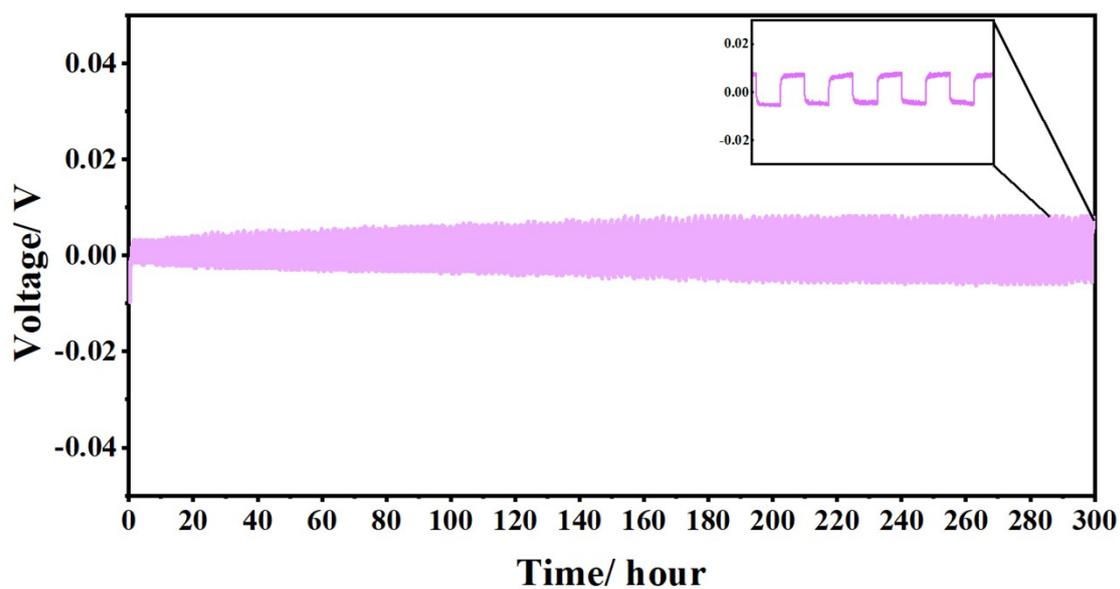


Figure S1. Voltage profile of Li|LiNO₃-KNO₃|Li symmetric cell using a current density of 1 mA·cm⁻² and a deposition/dissolution time for 1 h.

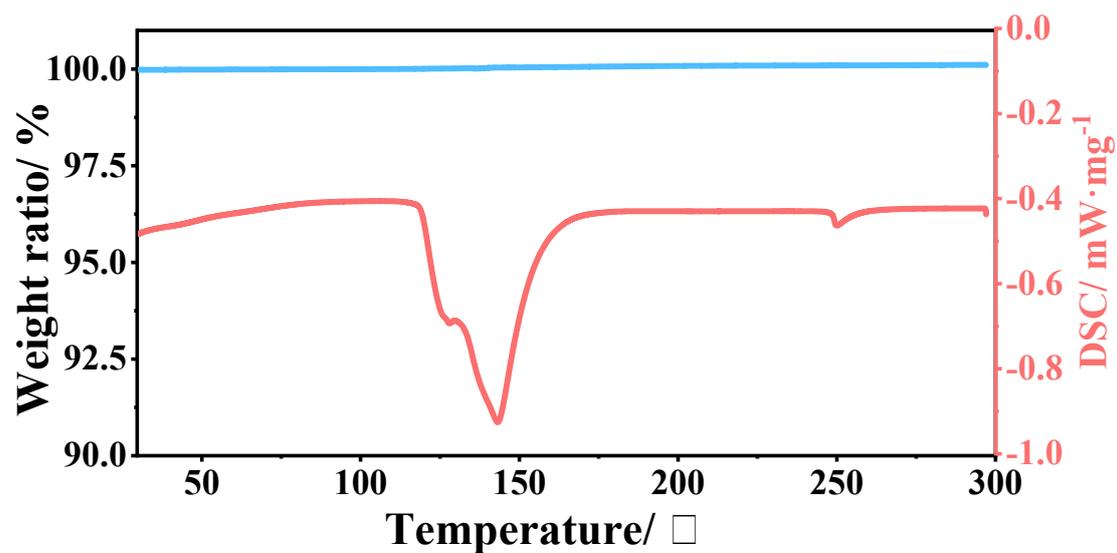


Figure S2. TGA result of the mixture of Li₂CO₃, KNO₃ and LiNO₃. Temperature range: 30 ~ 300 °C. Heating rate: 5 °C / min.

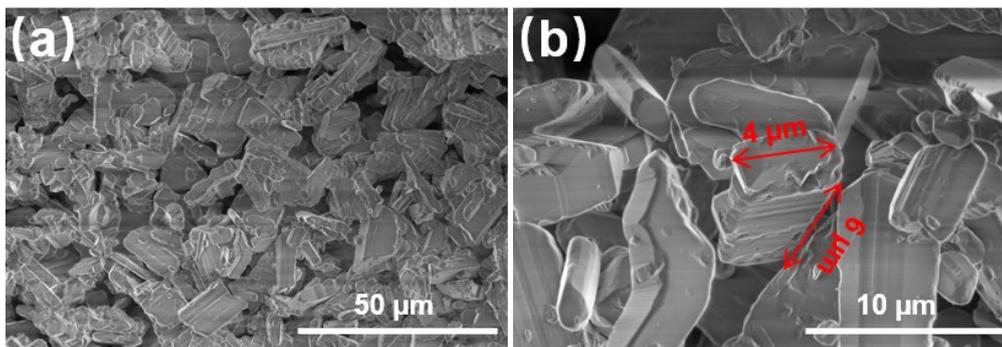


Figure S3. SEM images of the Li_2CO_3 power ordered from Alfa Aesar.

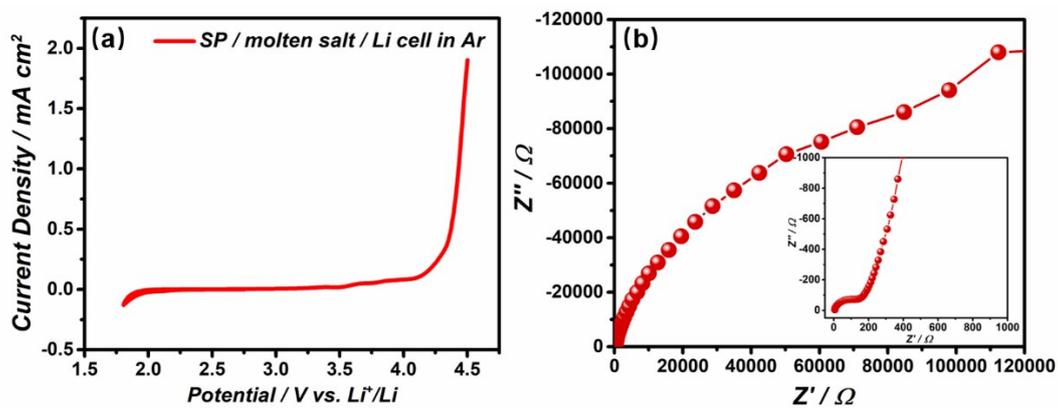


Figure S4. (a) Cyclic voltammogram curve of Super P electrode with molten salt electrolyte. Sweep rate: 1 mV s^{-1} ; (b) Nyquist plot of the molten salt electrolyte with two platinum plate electrodes ($1 \text{ cm} \times 1 \text{ cm}$) at $140 \text{ }^\circ\text{C}$.

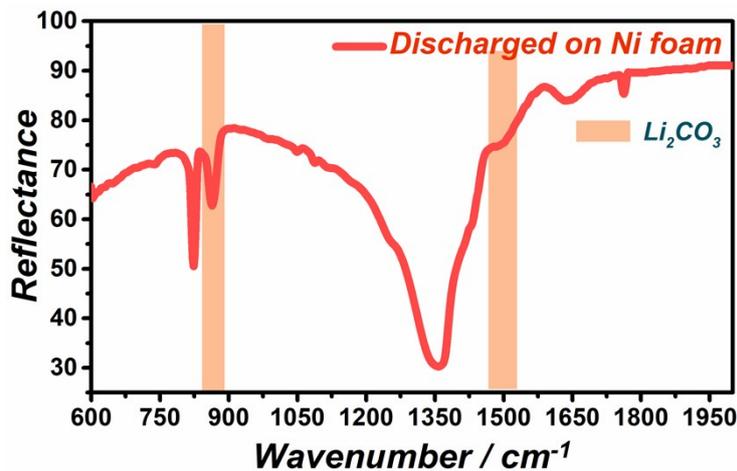


Figure S5. FT-IR of the discharged Ni foam cathode in $\text{LiNO}_3/\text{KNO}_3$ molten nitrate electrolyte at 100 mA g^{-1} . Herein, the Ni foam cathode was lifted immediately from the molten electrolyte when the discharging process completed. NMA solvent was employed to remove residual nitrate/nitrite salts on the surface of the Ni foam electrode.

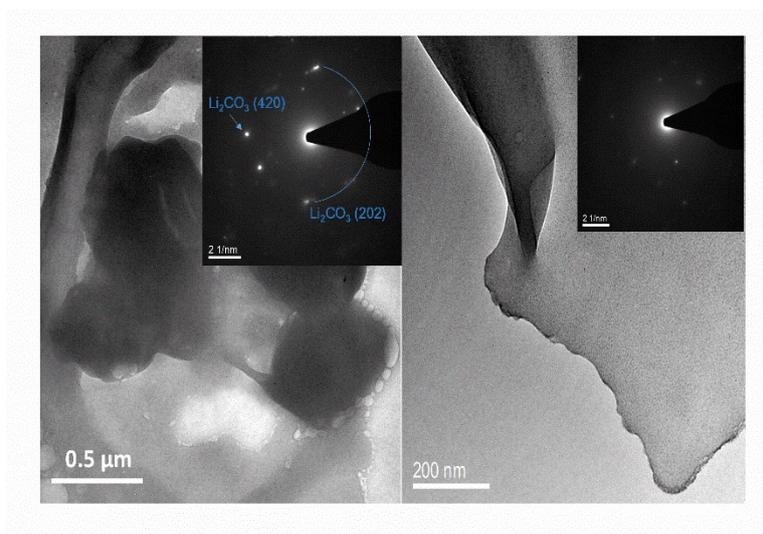


Figure S6. TEM images of the products from discharged Ni foam cathode in $\text{LiNO}_3/\text{KNO}_3$ molten nitrate electrolyte at 100 mA g^{-1} . Herein, the Ni foam cathode was lifted immediately from the molten electrolyte when the discharging process completed. For the preparation of TEM measurement, Ni foam electrode removed from the molten electrolyte was ultrasonic for 30 min in ethanol solvent in Ar atmosphere, after that, a few drops of the ethanol solvent were dripped onto the copper grid.

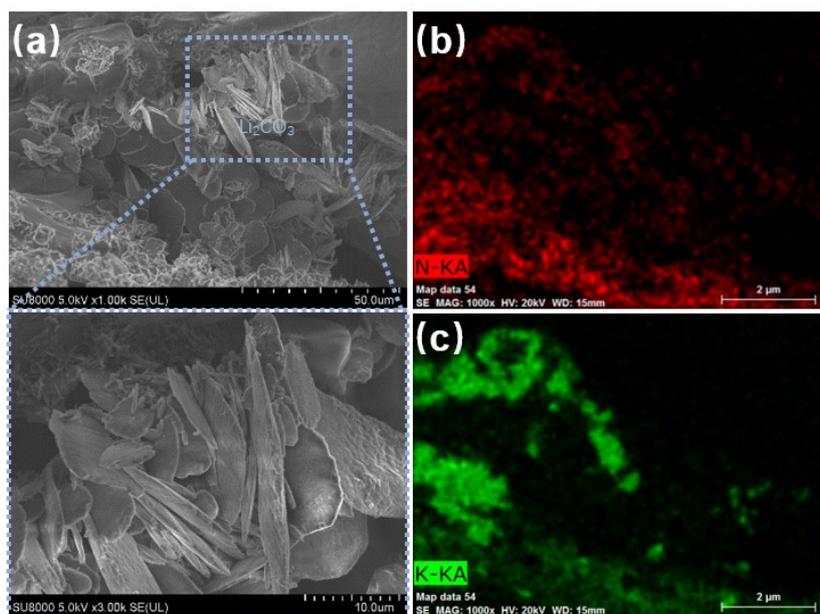


Figure S7. (a) SEM images of the Ni foam cathode (a); N (b) and K (c) element distribution images. In the region of the blue dotted line, neither K nor N was detected, flake particles in this region are speculated to be the discharge product of Li_2CO_3 .

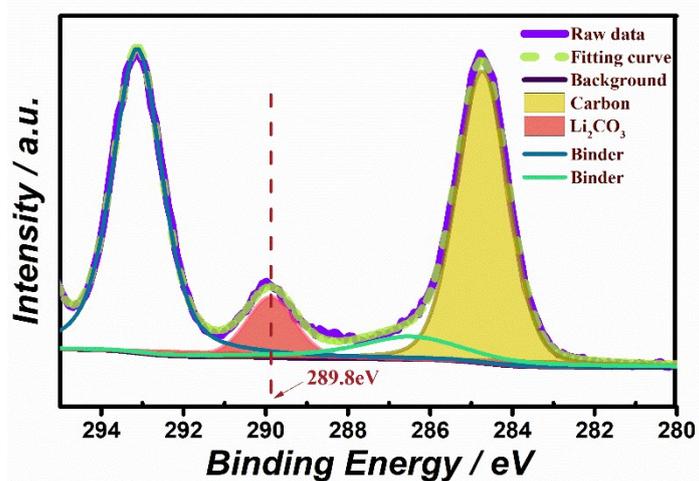


Figure S8. XPS spectra of the 30th recharged Super P cathode in $\text{LiNO}_3/\text{KNO}_3$ molten nitrate electrolyte at 100 mA g⁻¹. The peak corresponding to the C=O bond in Li_2CO_3 at 289 eV is detected, indicating that Li_2CO_3 formed during the discharge process cannot be completely oxidized after the subsequent recharge.

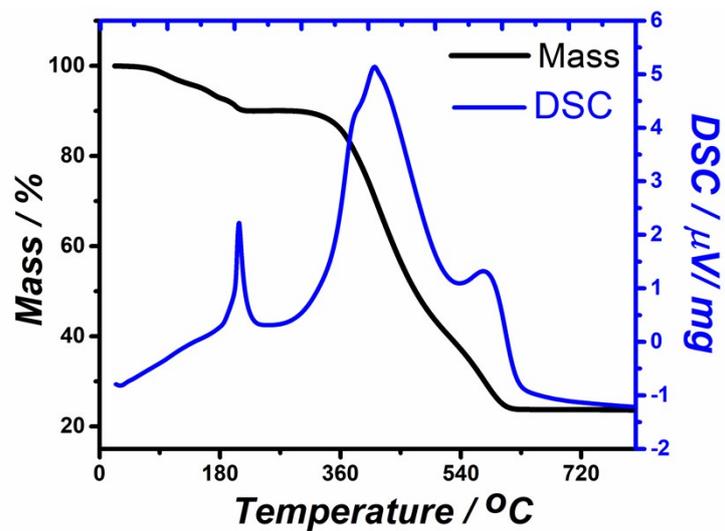


Figure S9. TG-DSC result of the Ru@Super P material. Temperature range: 25 ~ 800 °C. Heating rate: 5 °C / min.

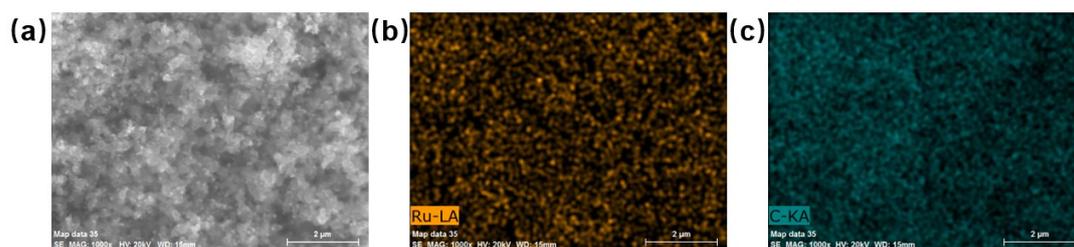


Figure S10. (a) SEM images of Ru@super P; Ru (b) and C (c) element distribution images.

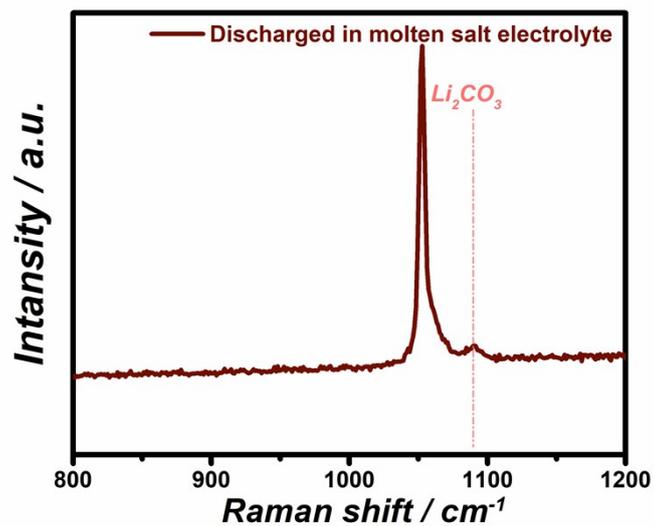


Figure S11. Raman result of the discharged Ru@Super P cathode in LiNO₃/KNO₃ molten nitrate electrolyte at 100 mA g⁻¹. Herein, the cathode was lifted immediately from the molten salt electrolyte when the discharging process completed.