

Supplementary Information

An inorganic molten salt electrolyte-based Li–CO₂ battery with moderate working temperature and enhanced performance

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Experimental section

Materials

As for components in the designed electrolyte, lithium bis(fluorosulfonyl)imide (LiFSI) was obtained from Suzhou Dodochem Ltd. and potassium bis(fluorosulfonyl)imide (KFSI) was purchased from TCI. What's more, lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) and tetraethylene glycol dimethyl ether (TEGDME) were gained from Sigma–Aldrich. All chemicals employed in synthesizing Ru@Super P were achieved from Aladdin. Super P carbon, Ni foam, and stainless steel (SS) current collector were obtained from Tianjin Evs Chemical Co., Ltd. Polytetrafluoroethylene (PTFE) binder was got from Macklin Inc. The glass fiber separator was acquired from GE Whatman. The salt was dried under vacuum at 120°C for 12 h, and the solvent was dried through molecular sieves prior to use. Super P carbon was grinded in the planetary ball mill for 8 h at 500 rpm. The preparation method of Ru@Super P was in accordance with the previous studies.^{1,2}

Electrolyte

The molten salt electrolyte was prepared by homogeneously milling LiFSI and KFSI mixture (molar ratio of 41:59) in an Ar-filled glove box with negligible H₂O and O₂ levels (<0.1 ppm). The organic electrolyte contains 1 M LiTFSI dissolved in TEGDME solvent.

Cathode

The cathode was prepared by rolling the mixture of Super P carbon (or Ru@Super P) and PTFE binder with a weight ratio of 85:15 into an even film and pressing on an SS mesh. The mass loading of each cathode was 0.2 ± 0.05 mg. All of the cathodes were dried for 12 h at 120°C under vacuum to remove adsorbed water.

Battery assembly

The as-prepared mixture electrolyte was firstly heated at 120°C, then GF/F glass fiber separator and Super P carbon (or Ru@Super P) cathode were impregnated in the eutectic mixture for at least 10 min. Subsequently, carbon cathode, glass fiber separator, and Li anode were assembled in a homemade Li–CO₂ mold battery, which was measured in a drying oven of 80°C. The Li–CO₂ battery containing Super P carbon cathode, GF/D glass fiber separator infiltrated with organic electrolyte, and Li

anode was operated at room temperature. The symmetric Li metal battery based on LiFSI–KFSI molten salt electrolyte was assembled using a coin-type mold with two Li electrodes.

Electrochemical measurements

The electrochemical impedance spectroscopy (EIS) of the eutectic mixture was conducted in an electrolytic cell with two Pt sheet electrodes (0.5 cm × 0.7 cm) separated by 2.5 cm. The fitting bulk resistance (R_b) and charge transfer resistance (R_{ct}) are 1953.1 Ω and 439.4 Ω , respectively. The ionic conductivity can be calculated as follows:

$$\sigma = \frac{d}{(R_b + R_{ct}) \times S} = \frac{2.5 \text{ cm}}{(1953.1 \Omega + 439.4 \Omega) \times 0.5 \text{ cm} \times 0.7 \text{ cm}} = 2.99 \times 10^{-3} \text{ S cm}^{-1}$$

In this formula, d is the distance between two Pt sheet electrodes, and S is the area of the Pt sheet electrode. EIS Nyquist plots of the molten salt electrolyte-based Li–CO₂ battery were also acquired from an impedance analyzer (Solartron 1287 coupled with Solartron 1260). The frequency range was from 1 MHz to 0.1 Hz, and the amplitude was 10 mV. Electrochemical window of the molten salt electrolyte was measured through linear sweep voltammetry (LSV) in a two-electrode configuration with an SS mesh cathode and a lithium foil anode under Ar. The LSV test was carried out on an electrochemical workstation (CHI440C, Chenhua Co., Shanghai, China). Galvanostatic discharge-charge measurements were performed on a LAND 2001A Battery Testing System (Wuhan, China) and a Neware Battery Test System (CT-4008T-5V10mA-164, Shenzhen, China).

Electrolyte, electrode and catalyst characterizations

The thermogravimetric (TG) measurement was performed to measure the melting point of the eutectic mixture and ascertain Ru content in the catalyst using an SDT Q600 TA instrument. Electrodes at various reaction stages and catalytic materials were analyzed by X-ray diffraction (XRD) using a Bruker D8 advanced diffractometer with Cu-K α radiation ($\lambda=1.5406 \text{ \AA}$). Raman spectra of electrodes were collected through a confocal microscope spectrometer (Renishaw inVia) employing a 50 \times long working distance lens (Leica Microsystems Inc.) and an excitation light of an air-cooled He–Ne laser at 633 nm wavelength. Chemical bonds analysis for cathode was conducted on a Fourier transform infrared (FTIR) spectroscope (PerkinElmer, Spectrum Two LiTa). The states of surface elements on the discharged Ni foam

cathode were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Model K-Alpha spectrometer) equipped with Al-K α radiation (1486.6 eV). The morphology of cathodes was observed through scanning electron microscopy (SEM, Hitachi SU8010). Moreover, the micro structure of Ru@Super P carbon was collected by transmission electron microscopy (TEM, FEI TF20), and corresponding SAED pattern was achieved from a Gatan charge-coupled device camera. In situ differential electrochemical mass spectrometry (DEMS) characterization was carried out in a home-made battery mold connected to the spectrometer chamber (PrismaPro QMG 250 M2) through a turbomolecular pump (Pfeiffer Vacuum). Ar gas was used as the carrier with a flux of 1 mL min⁻¹ during the electrochemical measurement process.

Supplementary figures

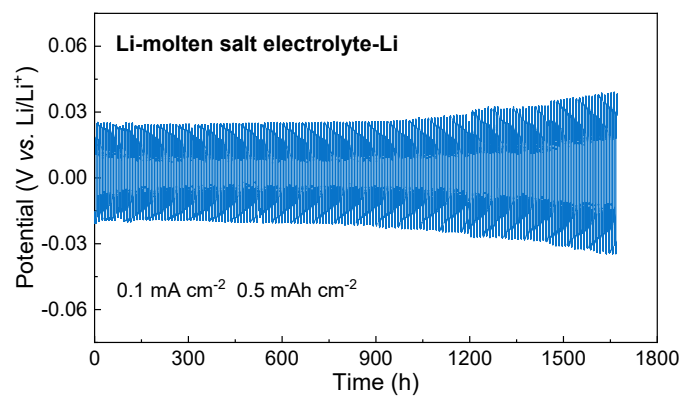


Fig. S1 The voltage profile of the symmetric Li metal battery based on LiFSI–KFSI molten salt electrolyte with a current density of 0.1 mA cm⁻² and deposition/stripping time for 5 h.

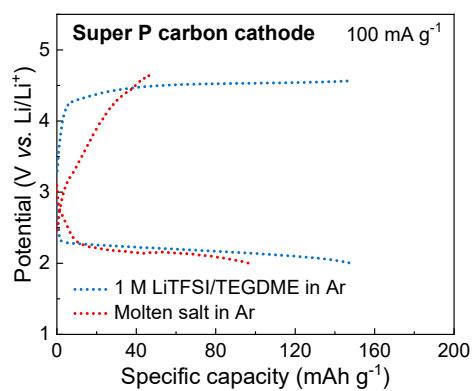


Fig. S2 Deep discharge and charge profiles on Super P carbon cathodes in 1M LiTFSI/TEGDME organic electrolyte and LiFSI–KFSI molten salt electrolyte under Ar at 100 mA g^{-1} .

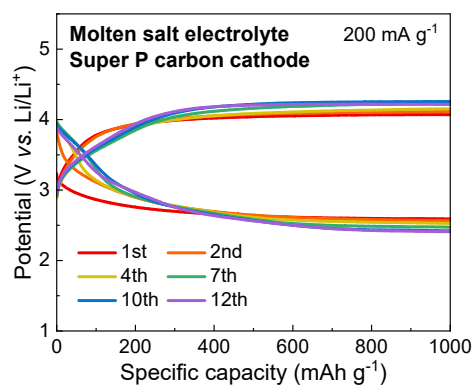


Fig. S3 Electrochemical cycling profiles of the Li-CO₂ battery containing LiFSI-KFSI molten salt electrolyte at a current density of 200 mA g⁻¹ and a cutoff capacity of 1000 mAh g⁻¹.

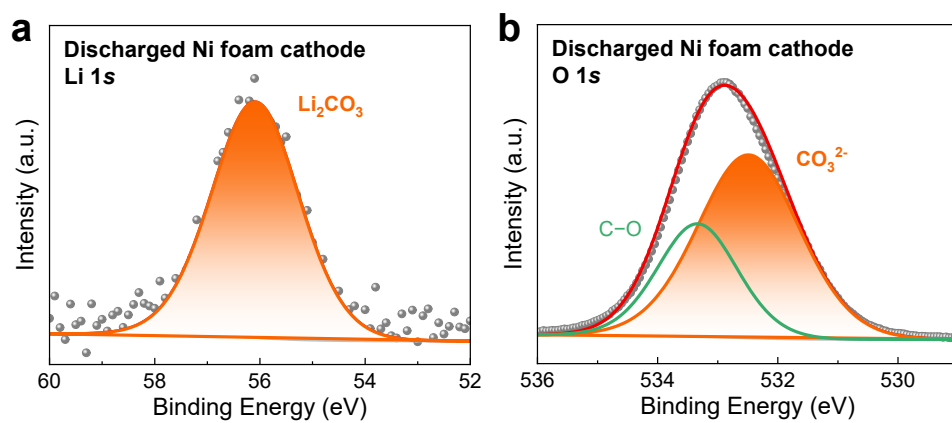


Fig. S4 (a) Li 1s and (b) O 1s XPS spectra of the discharged Ni foam cathode in the Li-CO₂ battery containing molten salt electrolyte.

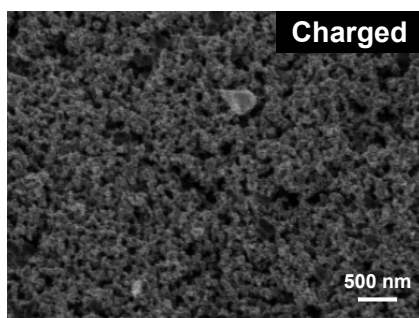


Fig. S5 SEM image of the Super P carbon cathode extracted from the Li-CO₂ battery after the recharge process.

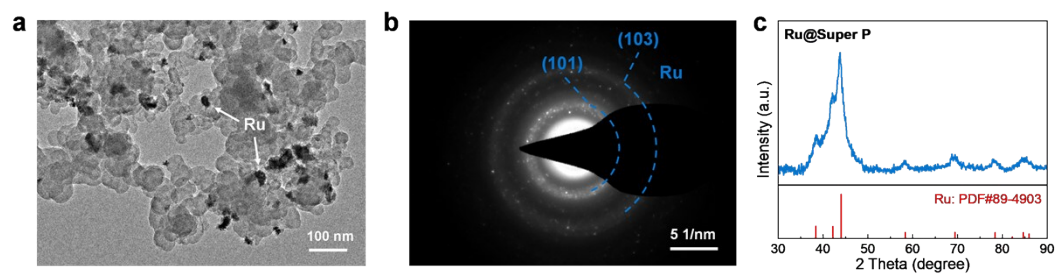


Fig. S6 (a) TEM image of the Ru@Super P carbon material. (b) SAED pattern of Ru nanoparticles. (c) XRD result of the Ru@Super P powder.

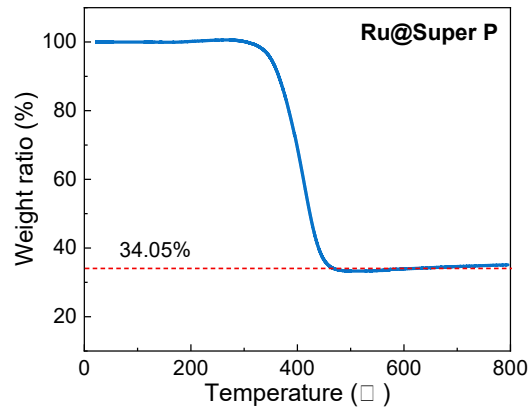


Fig. S7 TG curve of the Ru@Super P carbon material from room temperature to 800°C under O₂. The heating rate is 5°C min⁻¹.

The residual species is RuO₂ in the final state, whose mass fraction is 34.05%. The mass loading of Ru in Ru@Super P can be calculated as follows:

$$x_{Ru} = \frac{x_{RuO_2} \times M_{Ru}}{M_{RuO_2}} = \frac{34.05\% \times 101.07}{133.07} = 25.86\%$$

References

1. S. Yang, Y. Qiao, P. He, Y. Liu, Z. Cheng, J.-j. Zhu and H. Zhou, *Energy Environ. Sci.*, 2017, **10**, 972-978.
2. X. Sun, X. Mu, W. Zheng, L. Wang, S. Yang, C. Sheng, H. Pan, W. Li, C. H. Li, P. He and H. Zhou, *Nat. Commun.*, 2023, **14**, 536.