Electronic Supplementary Information (ESI)

Advanced Rechargeable Na-CO_2 Batteries Enabled by Ruthenium@Porous Carbon Composite Cathode with Enhanced Na_2CO_3 Reversibility

Luning Guo, Bing Li, Vediyappan Thirumal and Jiangxuan Song *

State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University

Xi'an 710049, China

Material preparation

All the materials were utilized as received without any treatment. $RuCl_3 \cdot nH_2O$ (Ru content 35%) was blended with ketjen black (mass ratio 1:2) by grinding in an agate mortar. The mixture was dispersed in ethylene glycol under ultrasonic for 15 minutes. The uniform suspension was refluxed at 180 ℃ for 5 hours. The suspension was cooled to room temperature and washed with ethanol and deionized water (volume ratio 1:1). Then the Ru@KB composite was achieved by drying the above mixture at 75℃ for 12h under vacuum.

Battery assembling and tests

The cathode was achieved as follows. The as-prepared Ru@KB composite and Polyvinylidene fluoride (PVDF) were blended (weight ratio 9:1) by ball-milling at speed of 350 rpm for 30 min in a solvent of NMP. Then the slurry was directly coated on the processed carbon paper and dried at 100℃ for 3h under vacuum. Hydrophobic carbon paper worked as current collector and substrate for cathode material, which was treated in an ultrasonic bath and cut into pieces with the diameter of 12 mm. The Na-CO_2 cell, which consisted of Na metal anode, glass fiber separator and the as-prepared composite cathode, was assembled in glove box filled with argon (H_2O and $O_2 \leq 0.1$ ppm). 80uL of 1M $NaClO_4$ dissolved in tetraethylene glycol dimethyl ether (TEGDME, Aldrich, 99%) was used as the electrolyte. The cell was tested in a home-made glass container filled with 1 atm CO_2 by CR2032 coin-type cell with the holey shell (Fig. S7). To make sure the CO_2 atmosphere for the cell, the glass container was directly taken out from glove box and then replace the Ar with 1atm CO_2 through Schlenk line. Electrochemical performance was carried out on the LAND-CT2001A Battery Testing System at 25℃. The specific

capacity was based on the Ru@KB composite loading on carbon paper, which was around 0.25 mg cm^{-2}.

Characterization

The crystalline structures were analyzed by Shimadzu XRD-6100 with Cu Kα radiation. Scanning electron microscope (SEM) images and element mapping were obtained on Techcomp SU3500 with energy dispersive spectrometer (EDS) detector. X-ray photoelectron spectroscopy (XPS) measurement was performed on Thermo Fisher Scientific ESCALAB Xi^+ with Al Kα radiation. Raman spectra were carried out on Laser Raman Spectrometer with 532 nm laser excitation. Transmission electron microscope (TEM) and corresponding element mapping were performed on JEM-2100Plus (JEOL).

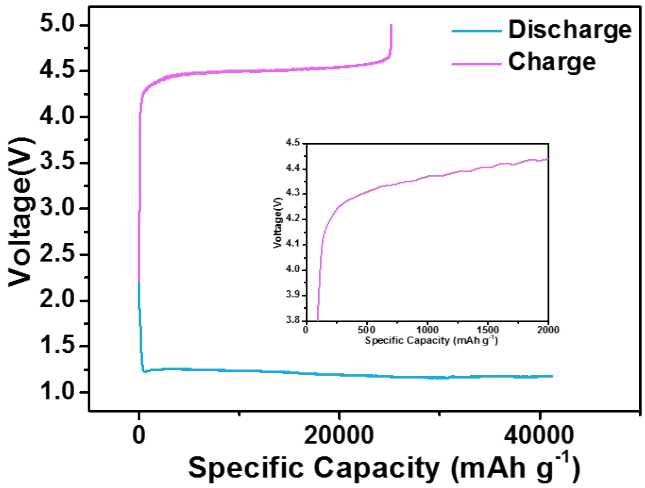

Fig. S1 Voltage profile of Na-CO_2 batteries operating in Ar atmosphere at a current density of 200 mA g^{-1}.

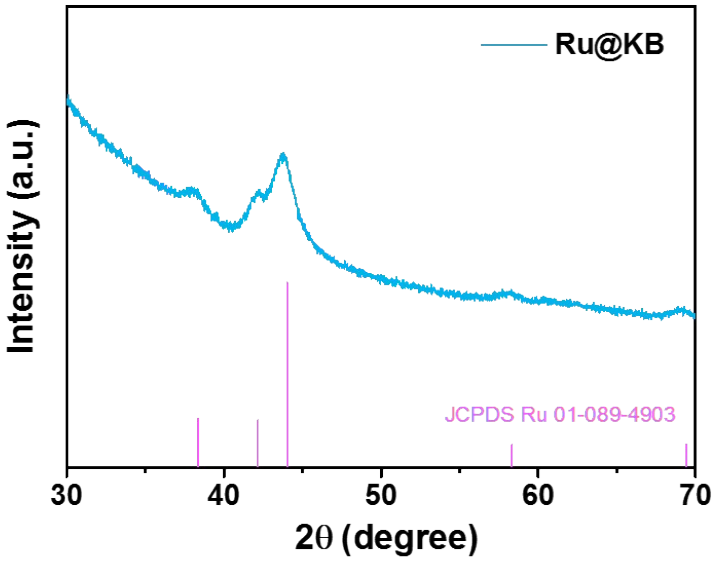

Fig. S2 XRD pattern of Ru@KB composite.

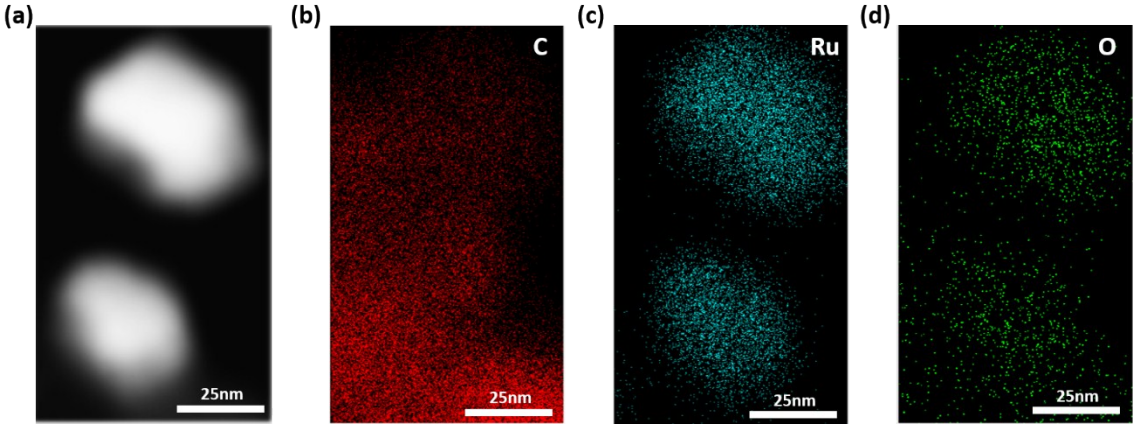

Fig. S3 EDS mapping of Ru@KB composite. (a) corresponding TEM image. (b) element C. (c) element Ru. (d) element O.

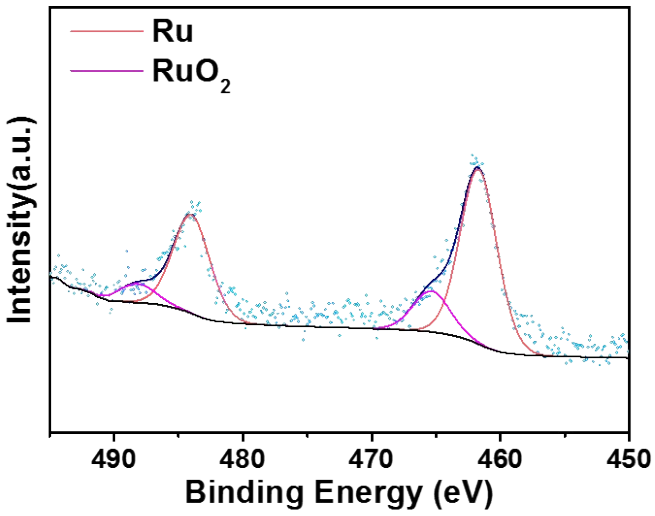

Fig. S4 Ru 3p XPS spectrum of the Ru@KB composite cathode before cycling.

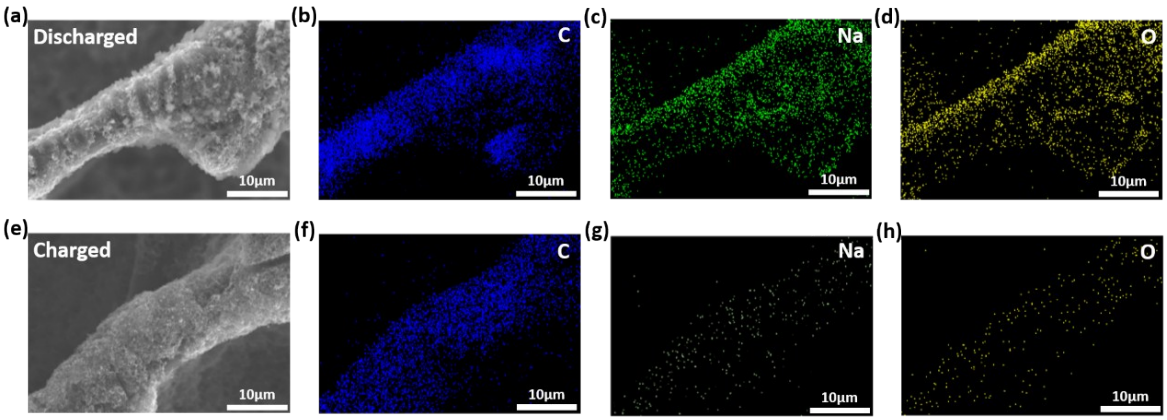

Fig. S5 SEM images of the cathode at different stages. (a) After discharge. (e) After recharge. Corresponding EDS mappings of the Ru@KB composite cathode after discharge. (b) element C. (c) element Na. (d) element O. Corresponding EDS mappings of the Ru@KB composite cathode after recharge. (f) element C. (g) element Na. (h) element O.

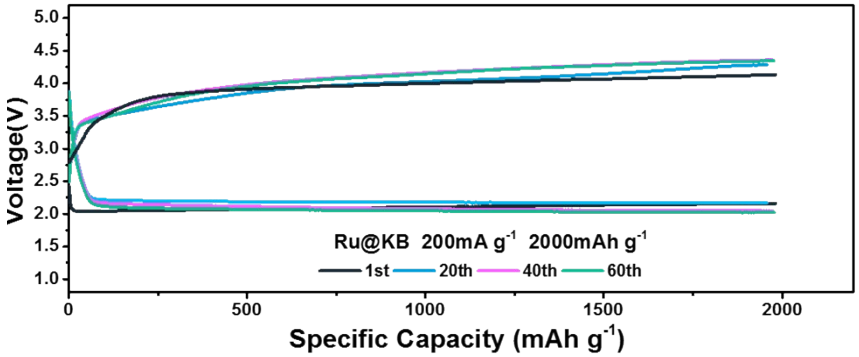

Fig. S6 Cycle performance of Na-CO_2 batteries with Ru@KB cathode at a current density of 200 mA g^{-1} with the cut-off capacity of 2000 mAh g^{-1}.

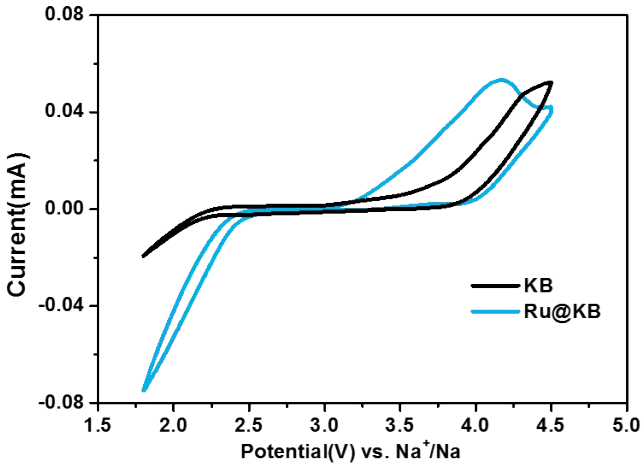

Fig. S7 Cyclic voltammograms of KB and Ru@KB electrodes under CO_2 atmosphere. Counter and reference electrodes: Na metal. Scan rate: 0.1 mV s^{-1}. Voltage window: 1.8–4.5 V versus Na/Na^+.

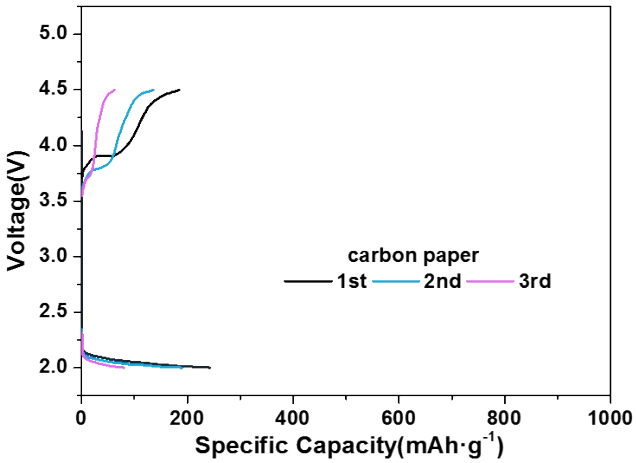

Fig. S8 Voltage profile of Na-CO2 batteries with carbon paper substrate cathode (without coating KB or Ru@KB) operating in CO_2 atmosphere.

Fig.S9 Picture of the home-made glass container.