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Jin, Yachao; Chen, Fuyi; Wang, Jiali; Johnston, Roy L.

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Tuning Electronic and Composition Effects in Ruthenium-Copper alloy Nanoparticles Anchored on Carbon Nanofibers for Rechargeable Li-CO₂ Batteries

Yachao Jin,[†] Fuyi Chen^{*,†}, Jiali Wang^{*,†} and Roy L. Johnston[#]

[†]State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an, 710072, China.

[#]School of Chemistry, University of Birmingham, Birmingham B15 2TT, UK

* Corresponding author: Tel./Fax: +86 029-88492052. E-mail: fuyichen@nwpu.edu.cn (Fuyi Chen), jialiwang@mail.nwpu.edu.cn (Jiali Wang)

ABSTRACT

Rechargeable Li-CO₂ batteries are attracting increasing attention due to their high energy density and ability to capture greenhouse gas CO₂. However, the difficulty in decomposing electronically insulating and electrochemically sluggish Li₂CO₃ discharge products under low charge voltages is still a major challenge. Herein, for the first time, a composite of intermixed ruthenium-copper alloy nanoparticles uniformly anchored on carbon nanofibers (*i*-RuCu/CNFs) as efficient cathode electrocatalysts for Li-CO₂ batteries is well designed. Remarkably, the Li-CO₂ batteries with *i*-Ru₄Cu₁/CNFs cathodes can be steadily cycled for over 110 cycles without capacity decay. And they show record-high rate capability along with much decreased overpotentials of 1.45 and 1.56 V even at current densities of 1000 and 2000 mA g⁻¹, respectively. Moreover, a high discharge capacity of 15753 mAh g⁻¹ is obtained for Li-CO₂ batteries based on *i*-Ru₄Cu₁/CNFs, and 99.3% of discharged capacity could be reversibly charged, giving the significant Coulombic efficiency. This work demonstrates the powerfully catalytic activity of intermixed RuCu nanoalloys for easily decomposing discharge

products in Li-CO₂ batteries and provides more insights to design more highly efficient cathode electrocatalysts for Li-CO₂ batteries and beyond.

Keywords: Li-CO₂ battery; intermixed RuCu nanoalloy; ultralow overpotential; superb rate capability

1. Introduction

Conversion of carbon dioxide (CO₂) to renewable energies in an environmental-friendly way has been considered as an appealing and essential approach for mitigating climate change and achieving sustainable development [1-3]. In recent decades, various routes have been investigated and employed to fulfill this purpose [4-7]. Li-CO₂ batteries represent one kind of novel and innovative technique that could coinstantaneously capture and convert CO₂ to electricity, differing from traditionally electrochemical reduction methods [8-11]. According to early researches, the work principle of Li-CO₂ batteries was proposed to comply with reversibly electrochemical reaction of $4\text{Li} + 3\text{CO}_2 \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$, which could theoretically deliver a high energy density of 1876 Wh kg⁻¹ [12, 13]. However, Li₂CO₃, as the main discharge product, is much thermodynamically stable, electronically insulating and electrochemically sluggish [14-16]. As a result, the difficulty of completely electrochemical decomposition of Li₂CO₃ within a low potential during the charge process seriously lowers energy efficiency and hinders deployment of Li-CO₂ batteries [17].

Electrocatalysts utilized to facilitate the kinetics of discharge and charge processes in Li-CO₂ batteries have been extensively studied [18], such as carbon nanomaterials [19, 20], transition metals [12, 15, 21-24], metal oxides [25, 26], metal carbides [27, 28] and redox mediator [29]. Zhang and co-workers introduced carbon nanotubes as cathode catalyst in rechargeable Li-CO₂ batteries [30], which showed a discharge capacity of 5786 mAh g⁻¹ and cycling performance of 20 cycles at current density of 100 mA g⁻¹. Ma et al. designed porous Mn₂O₃ cathode for Li-CO₂ batteries that delivered decreased discharge/charge voltage gap of

1.4 V at a current density of 50 mA g⁻¹ [25]. By comparison with carbon and metal oxide nanomaterials, transition metals as cathode catalyst usually exhibit better catalytic activity in Li-CO₂ batteries [31]. For example, Zhou's group reported that the reversible Li-CO₂ batteries with Ru@Super P as cathode showed excellent performance [12], which demonstrated a discharge capacity as high as 8229 mAh g⁻¹ and was discharged and charged for 80 cycles at current density of 100 mA g⁻¹. They elucidated that Ru is capable of promoting the reaction between Li₂CO₃ and C, optimizing charge route and lowering charge voltage compared to the pathway through self-decomposition of Li₂CO₃ [32]. Nevertheless, the pure monometallic Ru as cathode electrocatalyst displays very limited ability for catalyzing interactions between Li₂CO₃ and C for lack of promoting factors, such as geometric, compositional and electronic effects.

Currently, incorporating a second metal provides promising approach to energetically improve the catalytic activity over its monometallic analogue owing to the synergistic effects between two metals [33, 34], which has been considerably used in fields of catalysis [35], sensing [36] as well as Li-O₂ batteries [37]. Lu et al. designed PtAu/C bimetallic nanoparticles as bifunctional catalyst in Li-O₂ batteries [38], showing enhanced round-trip efficiency. They proposed that surface Au and Pt atoms are primarily responsible for ORR and OER kinetics in Li-O₂ batteries, respectively. Song and co-workers prepared PdCu bimetallic nanoparticles with mixed disordered fcc and ordered B2-type phases [39]. The resulting PdCu catalyst demonstrated superb round-trip efficiency of ~80% and cyclic stability for Li-O₂ batteries, which is ascribed to the weak LiO₂ adsorption strength caused by electron transfer from Cu to top-layer Pd atoms on the surface. More recently, the phase separated Ru-Cu nanoparticles on graphene was reported by Zhang et al. for improving Li-CO₂ battery performance [40]. Benefitting from synergistic effect between individual Ru and Cu nanoparticles, the Li-CO₂ batteries exhibited low overpotential and long cycle life. However, one can see that the Ru-Cu nanoparticles are not in the form of alloys. It is well-

known that solid solution phase of bimetallic alloy catalyst is usually more favorable to achieve the completely synergistic effects between two metal elements [41, 42]. So far, rare studies on catalytic decomposition of Li_2CO_3 using RuCu nanoalloys has been reported. Therefore, designing a intermixed RuCu nanoalloy cathode catalyst is highly desired to further greatly improve the performance for Li- CO_2 batteries.

Herein, we successfully designed and synthesized the intermixed ruthenium-copper single-phase solid solution nanoparticles that uniformly dispersed on carbon nanofibers (denoted as *i*-RuCu/CNFs) via a facile and effective solvothermal method although Ru and Cu are thermodynamically immiscible. Benefiting from the advantageous compositional and electronic effects between Ru and Cu, the Li- CO_2 batteries with *i*-RuCu/CNFs composite as cathodic electrocatalyst exhibit remarkably enhanced kinetics for CO_2 reduction and evolution. Our results show that the fabricated Li- CO_2 battery based on *i*- Ru_4Cu_1 /CNFs electrocatalyst demonstrates markedly low overpotentials of 1.45 and 1.56 V even at the current densities of 1000 and 2000 mA g^{-1} , respectively. What is more, such Li- CO_2 batteries can be steadily discharged-charged over 110 cycles at a large current density of 500 mA g^{-1} without the capacity decay. Notably, compared with the previously reported Ru-Cu nanoparticles with separated phase, the *i*- Ru_4Cu_1 /CNFs electrocatalyst shows more improved electrocatalytic performance for Li- CO_2 batteries. This work demonstrates the powerfully catalytic activity of intermixed RuCu nanoalloys for easily decomposing discharge products in Li- CO_2 batteries and provides more insights to design more highly efficient cathode electrocatalysts for Li- CO_2 batteries and beyond

2. Experimental Section

2.1 Chemicals

All chemical reagents used in experiments were analytical grade without any additional purification. Ruthenium chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$), copper chloride dihydrate

($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), ethylene glycol (EG), concentrated sulfuric acid (H_2SO_4), hydrochloric acid (HCl), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), sodium nitrate (NaNO_3) were bought from Sinopharm Chemical Reagent Co. Ltd. Lithium bis (trifluoromethane sulfonimide) (LiTFSI, 99.95%), Dimethylsulfoxide (DMSO, anhydrous, 99.9%) and carbon nanofibers (CNFs) were bought from Sigma-Aldrich. The Whatman separator was bought from GE Healthcare Life Sciences. Carbon paper was bought from the Fuel Cell Store. Ultrapure water with the resistance of $18.25 \text{ M}\Omega \text{ cm}$ was used in this experiment.

2.2 Synthesis of the intermixed RuCu/CNFs nanoalloy electrocatalysts

The CNFs were firstly oxidized according to a modified Hummers method [43, 44]. Then, the oxidized CNFs were taken as substrates to synthesize the intermixed RuCu nanoalloys through the solvothermal method. Taking *i*- $\text{Ru}_4\text{Cu}_1/\text{CNFs}$ composite as the sample, the oxidized CNFs (50 mg) was mixed with EG (50 mL) containing $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (8 mM) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mM) in a 100 mL baker to form a homogeneous solution under the help of ultrasonication. Subsequently, this solution was allowed to stir overnight. The total precursor concentration is a constant value of 10 mM. Then, the resulting solution was transferred to a 100 mL Teflon-lined autoclave and heated at 180°C for 10 h. After natural cooling down to room temperature, the black precipitates were collected and washed by ethanol and ultrapure water several times, and dried via the freeze-dried process overnight. The obtained products were further heat treated under the argon gas at 350°C for 2h for the final *i*- $\text{Ru}_4\text{Cu}_1/\text{CNFs}$ nanomaterials. Accordingly, the other electrocatalysts including *i*- $\text{Ru}_5\text{Cu}_1/\text{CNFs}$, *i*- $\text{Ru}_3\text{Cu}_1/\text{CNFs}$, *i*- $\text{Ru}_1\text{Cu}_1/\text{CNFs}$, Ru/CNFs and Cu/CNFs were prepared by using the same method with only changing the metal precursor concentration. The Ru_xCu_y was assigned based on the precursor ratio of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The carbon-free *i*- Ru_4Cu_1 nanomaterials were prepared by using the same method as that of preparing *i*-

Ru₄Cu₁/CNFs nanomaterials only without the addition of CNFs substrates, which were subsequently coated on the Ni foam with a layer of Au film for the carbon-free cathode electrodes.

Furthermore, the nanomaterials that Ru and Cu nanoparticles separately dispersed on CNFs with separated phase (referred to as *s*-Ru₄-Cu₁/CNFs hereafter) were also prepared based on the method of preparing *i*-Ru₄Cu₁/CNFs with modification. Briefly, the oxidized CNFs (50 mg) was mixed with EG (50 mL) containing the RuCl₃·nH₂O (8 mM). Then the resulting homogeneous solution was heated at 180 °C for 10 h in a 100 mL Teflon-lined autoclave. After cooling down, the precipitates were collected and washed by ethanol and ultrapure water several times, and were then re-dispersed into the EG (50 mL) containing CuCl₂·2H₂O (2 mM). Subsequently, the resulting solution was allowed to stir overnight and transferred to a 100 mL Teflon-lined autoclave for reaction at 180 °C for 10 h. After cooling down, the precipitates were collected and washed, and dried via the freeze-dried process overnight. The obtained products were further heat treated under the argon gas at 350 °C for 2h for the final *s*-Ru₄-Cu₁/CNFs nanomaterials.

2.3 Physical characterization

Transmission electron microscope (TEM) and High-resolution TEM (HRTEM) images were obtained with a FEI Talos F200X (USA) operated at 200 kV. High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images and elemental mappings were recorded using TEM coupled with energy-dispersive X-ray spectroscopy (EDS). Scanning electron microscope (SEM) images were obtained on a FEI Helios G4 CX (USA). X-ray diffraction (XRD) patterns were performed on a PANalytical X'Pert Pro MPD with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The accelerating voltage and current employed were 40 kV and 40 mA, respectively. The compositional ratio were determined by inductively coupled plasma-mass spectrometry (ICP-MS, NexION 350D) and X-Ray fluorescence spectroscopy

(XRF, Bruker S8 Tiger). X-ray photoelectron spectroscopy (XPS) was carried out with an ESCALAB 250 instrument under the ultrahigh vacuum of 10^{-9} Torr using monochromated Al K α radiation ($h\nu = 1486.6$ eV), all binding energies were calibrated by the carbon peak (C 1s) at about 284.5 eV. The Fourier transform infrared spectra (FTIR, Bruker vertex 80) were performed to analyse the discharge/charge processes. The Raman spectra (WITec, Alpha300R) and gas chromatography (GC, Techcomp, GC7900) were taken to study the discharge products and gas emission during the cycling process. The discharged/charged cathode electrodes were washed three times by dimethylsulfoxide (DMSO) to remove the residue Bis(trifluoromethane)sulfonimide (LiTFSI) salt before the characterization of XRD, SEM, TEM, XPS, FTIR and Raman. The mass of metal was determined by thermogravimetric analysis (TGA) measurements (Netzsch).

2.4 Assembly of Batteries and measurements

The cathodic electrodes of Li-CO₂ batteries were prepared via a slurry. Typically, 5 mg of obtained electrocatalyst with 10% PVDF binder were dispersed in 1 mL of the N-methyl pyrrolidone (NMP) to form a homogeneous slurry under the help of ultrasonication. Then, such slurry was coated on a carbon paper (10 mm in diameter) with the loading amount of 0.2 mg as the cathodic electrode. The obtained cathodic electrodes were further dried at 80 °C overnight under vacuum. The lithium-metal chips (diameter: 15.6 mm, thickness: 0.25 mm) and the glass fiber separator (Whatman, diameter: 19 mm) were used as the anodic electrode and separator, respectively. The electrolyte used in this research is 1 M LiTFSI dissolved in the DMSO solution. Finally, the 2032 coin-type cells with the holes on the cathode side were taken to fabricate the Li-CO₂ batteries in a glovebox filled with high-purity argon gas. The as-prepared coin cells were sealed into the home-made chamber filled with pure CO₂. On the other hand, the Li-O₂/air batteries were prepared same as that of Li-CO₂ batteries, which were sealed into the home-made chamber filled with pure O₂ or dry air, respectively. To monitor the gas emission of Li-CO₂ batteries during the charge process, the customized Swagelok-type

Li-CO₂ batteries were also fabricated. The Li-CO₂ battery properties were measured in a LAND cycler (Wuhan Land Electronic Co. Ltd). The capacity values were normalized by the mass of electrocatalyst in cathodic cathodes. The overpotentials of Li-CO₂ batteries were calculated by voltages difference at the middle of the charge/discharge plateaus.

3. Results and discussion

3.1 Physcial characterization of *i*-Ru₄Cu₁/CNFs

The phase structures of resulting nanomaterials were initially examined by X-ray diffraction (XRD) pattern. As illustrated in Fig. 1a, the typical Bragg peaks attributing to hexagonal Ru are clearly observed for both *i*-Ru₄Cu₁/CNFs and Ru/CNFs [45, 46], with the peak at 25° associated to the (002) diffraction peak of CNFs substrates. Compared with the XRD pattern of Cu/CNFs (Fig. S1), one can see no other additional peaks for Cu in *i*-Ru₄Cu₁/CNFs. Moreover, the diffraction peaks of *i*-Ru₄Cu₁/CNFs shifted to higher angles compared to those of Ru/CNFs, which can be ascribed to the incorporation of Cu atoms into the Ru crystal lattice without changing the crystal structure and an indicative of formation of hexagonal close-packed (hcp) *i*-Ru₄Cu₁ nanoalloy [47, 48]. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques were performed to investigate the morphologies and nanostructures of *i*-Ru₄Cu₁/CNFs (Fig. S2 and Fig. 1b, c). Obviously, sphere-shaped *i*-Ru₄Cu₁ nanoalloys with diameters ranging from 5 to 15 nm are uniformly distributed on the CNFs surfaces. High-resolution TEM (HRTEM) image shown in Fig. 1d displays the continuous lattice fringes, indicating the highly crystalline nature of *i*-Ru₄Cu₁ nanoalloys. The confirmed lattice fringe distance of 0.226 nm (Fig. 1e and Fig. S3c) are ascribed to the (100) plane of *i*-Ru₄Cu₁ nanoalloy [45, 47], which reveals a lattice contraction compared to that of pure Ru owing to the formation of *i*-Ru₄Cu₁ nanoalloy, consistent well with the XRD result. The high-angle annular dark-field scanning TEM (HAADF-STEM) image in conjunction with energy-dispersive X-ray spectroscopy (EDS)

profile illustrate that Ru and Cu elements are distributed evenly in each nanoparticle (Fig. 1g-i, Fig. S4). The EDS line-scan profile recorded in a single nanoparticle further verifies the formation of homogeneous *i*-Ru₄Cu₁ nanoalloys (Fig. 1j). To precisely determine the atomic compositions of Ru and Cu in *i*-Ru₄Cu₁ nanoalloy, the inductively coupled plasma-mass spectrometry (ICP-MS) and X-Ray fluorescence spectroscopy (XRF) as well as EDS were conducted [49, 50]. The atomic percentage of Ru and Cu were measured to be 80.2% Ru and 19.8% Cu in *i*-Ru₄Cu₁ nanoalloy (Table S1 and Fig. S5), respectively, which is in good accordance with the feeding ratio of precursor solution. Furthermore, the mass proportion of *i*-Ru₄Cu₁ nanoalloy and CNFs substrate in *i*-Ru₄Cu₁/CNFs nanomaterial measured by thermogravimetric analysis (TGA) are 38.3% and 61.7%, respectively (Fig. S6).

X-ray photoelectron spectroscopy (XPS) analysis was employed to investigate the chemical valences and electronic interactions of Ru and Cu in *i*-Ru₄Cu₁/CNFs. As shown in Fig. 2a, the survey spectrum of *i*-Ru₄Cu₁/CNFs exhibits the clear characteristic peaks for Ru and Cu, and the atomic percentage of Ru and Cu on catalyst surface was determined to be 82.2 and 17.8, respectively. Combined with the consistent ICP-MS results, it is concluded that Ru and Cu are uniformly distributed in both bulk and surface, confirming the homogeneous *i*-Ru₄Cu₁ nanoalloys. As determined by the high-resolution XPS spectra of Ru (Fig. 2b and Fig. S7), the binding energy of 461.4 (Ru 3_p_{3/2}) and 483.6 eV (Ru 3_p_{1/2}) are attributed to Ru⁰, while the binding energy of 464.2 (Ru 3_p_{3/2}) and 484.2 eV (Ru 3_p_{1/2}) are assigned to the presence of Ru⁴⁺ [51-53], emphasizing that Ru in *i*-Ru₄Cu₁/CNFs are mainly present in metallic state. More importantly, it is noted from Fig. 2b that the XPS core-level spectra of Ru 3_p in *i*-Ru₄Cu₁/CNFs displays a negative shift with respect to those of Ru/CNFs, indicating charge transfer from Cu to Ru due to the higher electronegativity of Ru [54], which can be further confirmed by the positive shift of core-level spectra of Cu 2_p in *i*-Ru₄Cu₁/CNFs compared with that in Cu/CNFs (Fig. 2c). The binding energy located at 952.4 (Cu 2_p_{1/2}) and 932.6 eV (Cu 2_p_{3/2}) are indicative of Cu⁰, whereas the peaks centered at 953.8 (Cu 2_p_{1/2}) and 934 eV

(Cu $2p_{3/2}$) are attributed to Cu^{2+} in *i*- $\text{Ru}_4\text{Cu}_1/\text{CNFs}$ [55, 56]. One can see that the complete alloying between Ru and Cu effectively reduces the Cu oxidation, which is favorable for electrocatalytic process. Moreover, as shown in Fig. S8, with increasing Cu contents in *i*- RuCu/CNFs , the binding energy of Ru $3p$ was observed to continuously shift to lower values, demonstrating the gradual alloying and robust electronic interactions between Ru and Cu. To prove this phenomenon, the valence band spectra (VBS) was further performed to study the electronic structure. Fig. 2d exhibits an effective downshift of the d-band center in *i*- $\text{Ru}_4\text{Cu}_1/\text{CNFs}$ relative to that of pure Ru/CNFs . Such advantageous modification of electronic structure indicates the promising potential of *i*- $\text{Ru}_4\text{Cu}_1/\text{CNFs}$ for greatly improved catalytic activities [57].

3.2 Performance of Li- CO_2 battery based on *i*- $\text{Ru}_4\text{Cu}_1/\text{CNFs}$ electrocatalyst

Then, we systematically evaluated the electrochemical performance of *i*- $\text{Ru}_4\text{Cu}_1/\text{CNFs}$ as cathodes for Li- CO_2 batteries. As shown in Fig. 3a, the Li- CO_2 battery based on *i*- $\text{Ru}_4\text{Cu}_1/\text{CNFs}$ shows the lowest charge-discharge overpotential of 0.9 V coupling with reduced charge voltage of 3.7 V at a constant current density of 100 mA g^{-1} . However, the Li- CO_2 batteries with Ru/CNFs , Cu/CNFs and CNFs as cathode electrocatalysts display much higher charge-discharge overpotentials (1.32, 1.46 and 1.59 V, respectively) and charge voltages (4.03, 4.14 and 4.22 V, respectively) (Fig. 3b, Fig. S9 and Fig. S10). These results indicate that the battery performance obtained by *i*- $\text{Ru}_4\text{Cu}_1/\text{CNFs}$ cathode is remarkably improved by alloying Ru with Cu, even much superior to that of Li- CO_2 batteries based on phase separated Ru-Cu nanoparticles and most previously reported Li- CO_2 batteries (Table S2) [15, 21, 22, 25]. Besides, the various *i*- RuCu/CNFs nanomaterials with different Ru and Cu atomic ratios have also been prepared and used to fabricate corresponding Li- CO_2 batteries. As shown in Fig. S11, with the gradual increase of Cu contents in various *i*- RuCu/CNFs electrocatalysts, the properties of their Li- CO_2 batteries have been

correspondingly changed. Attractively, the Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs electrocatalyst demonstrates the lowest charge-discharge overpotential, revealing that the kinetics of discharge and charge processes in Li-CO₂ batteries are successfully accelerated by the bimetallic *i*-Ru₄Cu₁/CNFs nanoalloys with the optimized Ru/Cu atomic ratio. Therefore, the *i*-Ru₄Cu₁/CNFs electrocatalyst is chosen for the further research. Recent researches have demonstrated that Ru is an excellent candidate for promoting interaction between Li₂CO₃ and C during charge process through the reversibly electrochemical reaction of $2\text{Li}_2\text{CO}_3 + \text{C} \leftrightarrow 4\text{Li} + 3\text{CO}_2$ [12], which is a highly favorable pathway to particularly decrease charge voltage of Li-CO₂ batteries. In this work, the bimetallic *i*-Ru₄Cu₁/CNFs nanoalloy possesses the effectively modified electronic structure, as manifested in the downshift of d-band center, resulting in a favorable binding of Li₂CO₃ [54, 57], which is more beneficial for accelerating reaction between Li₂CO₃ and C [40]. Therefore, the reaction kinetics of Li₂CO₃ formation and decomposition are further facilitated by the bimetallic *i*-Ru₄Cu₁/CNFs. Whereas, such effect is not obtained for Li-CO₂ batteries with monometallic Ru/CNFs and Cu/CNFs electrocatalysts.

Furthermore, in practical Li-air batteries, Li₂CO₃ is still one of the major by-products that deteriorates battery properties, causing high charge voltage and poor cyclability [58]. Hence, to achieve high performance of practical Li-air batteries, it is essential to decrease the decomposition voltage of Li₂CO₃. Fortunately, the bimetallic *i*-Ru₄Cu₁/CNFs prepared in this work has demonstrated excellent capability to decompose Li₂CO₃ at low charge voltage in Li-CO₂ batteries. By using *i*-Ru₄Cu₁/CNFs as cathodic electrocatalyst, the Li-air batteries shows not only the enhanced discharge voltage of 2.94 V but also the decreased charge voltage, as for the Li-CO₂ batteries based on *i*-Ru₄Cu₁/CNFs (Fig. 3c and Fig. S12), indicating the effectiveness of the bimetallic *i*-Ru₄Cu₁/CNFs for improving the performance of Li-air batteries. In addition, the *i*-Ru₄Cu₁/CNFs was further subjected to test the long-term stability of Li-CO₂ battery cycled at a current density of 500 mA g⁻¹ with limited capacity of 1000 mAh g⁻¹. As shown in Fig. 3d, it is noteworthy that Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs

displays a superb cycling performance for more than 110 cycles with much high discharge voltages (Fig. 3e), in a sharp contrast, Li-CO₂ battery based on Ru/CNFs can only survive to 43 cycle at the identical condition. The time-voltage curves also clearly confirms that the Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs illustrates more stable cyclability with dramatically increased discharge and decreased charge voltages than that based on Ru/CNFs (Fig. 3f). Moreover, the cycling performance of the Li-CO₂ batteries based on various *i*-RuCu/CNFs electrocatalysts with different atomic ratios were also systematically examined. As illustrated in Fig. S13, the Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs electrocatalyst reveals the most excellent cycling performance, further confirming that the *i*-Ru₄Cu₁/CNFs electrocatalyst represents the optimal component in *i*-RuCu/CNFs system for improving the Li-CO₂ battery properties. More importantly, with continuously increasing the discharge-charge current density to 1000 mA g⁻¹ during cycling process, the Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs can still be stably cycled for 120 cycles with negligible decay (Fig. S14).

The rate capability of Li-CO₂ batteries was characterized at different current densities ranging from 100 mA g⁻¹ to 2000 mA g⁻¹. As shown in Fig. 4a, the discharge voltages of the Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs are higher than those of Ru/CNFs counterparts over the whole range of current densities. Unexpectedly, the Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs delivers remarkably low overpotentials of 1.45 and 1.56 V even at much high current densities of 1000 and 2000 mA g⁻¹ (Fig. 4b and c), respectively. The discharge voltage at 2000 mA g⁻¹ still reach to 2.62 V, representing the best rate capability ever reported [13, 23, 40]. By contrast, the discharge voltages of Li-CO₂ battery based on monometallic Ru/CNFs decrease drastically as current density was increased to 1500 mA g⁻¹, which further drop to cutoff voltage of 2 V when current density is 2000 mA g⁻¹ (Fig. S15). In addition, the overpotentials of Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs are much lower than those of Li-CO₂ battery based on Ru/CNFs at all current densities (Fig. 4b). The Li-CO₂ battery based on

i-Ru₄Cu₁/CNFs displays a round-trip efficiency as high as 76 % at current density of 100 mA g⁻¹ (Fig. S16), outperforming the corresponding value of 67.5 % for Ru/CNFs counterpart.

The full discharge-charge curves of Li-CO₂ batteries were carried out at current density of 300 mA g⁻¹. Fig. 4d shows a discharge capacity of 15753 mAh g⁻¹ for Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs. The discharge-charge cycle is almost completely reversible with a Coulombic efficiency as high as 99.3% (cutoff charge voltage at 4.2 V). Under the same testing conditions, however, the discharge capacity of Li-CO₂ battery based on Ru/CNFs is only 8580 mAh g⁻¹, much lower than that of Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs, with only 34% of the discharged capacity being reversibly charged to the cutoff voltage. Besides, we also investigated the effect of *i*-Ru₄Cu₁ mass loading in *i*-Ru₄Cu₁/CNFs electrocatalysts on the batteries performance. Interestingly, when the mass loading of *i*-Ru₄Cu₁ nanoalloy in *i*-Ru₄Cu₁/CNFs electrocatalyst was changed to a lower or higher value (Fig. S17), their discharge capacities are both decreased (Fig. S18) [59], indicating that the *i*-Ru₄Cu₁/CNFs with the appropriate metallic mass loading of 38.3% would favorably accelerate the Li-CO₂ battery performance .

The above systematically electrochemical studies powerfully demonstrate that the properties of Li-CO₂ batteries have been remarkably promoted by using the bimetallic *i*-Ru₄Cu₁/CNFs electrocatalysts, which is attributed to the formation of *i*-Ru₄Cu₁ solid solution nanoalloys with the favorable electronic structure. Importantly, to more clearly elucidate the alloying effect in *i*-Ru₄Cu₁/CNFs for improving the Li-CO₂ batteries performance, the *s*-Ru₄-Cu₁/CNFs electrocatalysts that Ru and Cu nanoparticles separately dispersed on CNFs with the separated phase were further prepared in this work (Fig. S19). As shown in Fig. S20, it is noted that the Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs electrocatalyst displays much lower charge-discharge overpotentials than that of Li-CO₂ battery based on *s*-Ru₄-Cu₁/CNFs electrocatalyst at all current densities ranging from 100 to 2000 mA g⁻¹, confirming that the *i*-

$\text{Ru}_4\text{Cu}_1/\text{CNFs}$ with well-defined solid solution phase could further promote the kinetics of discharge and charge processes for enhancing Li-CO_2 batteries performance relative to that of $s\text{-Ru}_4\text{-Cu}_1/\text{CNFs}$ with separated Ru and Cu nanoparticles dispersion. The main reason can be rationally explained that the $i\text{-Ru}_4\text{Cu}_1/\text{CNFs}$ electrocatalysts with solid solution phase remarkably facilitate the charge transfer between the two different atoms owing to the intimate interactions among these heteroatoms in a solid solution phase compared to that electrocatalysts with separated nanoparticles dispersion. Eventually, the electronic structure of such bimetallic $i\text{-Ru}_4\text{Cu}_1/\text{CNFs}$ nanoalloys are precisely modified at the atomic level for well tuning the electrochemical properties [50, 60, 61].

3.3 Analysis of $i\text{-Ru}_4\text{Cu}_1/\text{CNFs}$ cathode electrode after discharge-charge processes

To investigate the discharge products and reversibility of Li-CO_2 battery based on $i\text{-Ru}_4\text{Cu}_1/\text{CNFs}$, systematical characterizations were further carried out. Fig. 5a presents the XRD patterns of $i\text{-Ru}_4\text{Cu}_1/\text{CNFs}$ cathodes after full discharge and charge. The obvious diffraction peaks ascribed to Li_2CO_3 were observed on discharged $i\text{-Ru}_4\text{Cu}_1/\text{CNFs}$ electrode, indicating the formation of Li_2CO_3 discharge products [13]. After recharging such Li-CO_2 battery, the diffraction peaks of Li_2CO_3 disappear, uncovering the highly reversible formation and decomposition of crystalline Li_2CO_3 promoted by the $i\text{-Ru}_4\text{Cu}_1/\text{CNFs}$ during discharge-charge processes, which is in accordance with its high Coulombic efficiency. The XPS spectrum of C 1s for discharged $i\text{-Ru}_4\text{Cu}_1/\text{CNFs}$ electrode shows a new peak at 289.9 eV with much strong intensity, which is assigned to Li_2CO_3 (Fig. 5b) [62, 63]. Moreover, the peak at 280.16 eV in terms of Ru 3d disappears on such discharged $i\text{-Ru}_4\text{Cu}_1/\text{CNFs}$ electrode owing to the deposition of discharge products on electrode surface. Intriguingly, after recharging, the XPS peak associated with Li_2CO_3 is nearly eliminated with a much faint signal, while the peak representing Ru 3d reappears (Fig. 5c), which confirms that Li_2CO_3 can be almost reversibly decomposed, allowing the release of CO_2 and storing electricity again. Similarly,

the Fourier transform infrared spectra (FTIR) of fully discharged and charged *i*-Ru₄Cu₁/CNFs electrodes also show the reversible generation and vanishment of Li₂CO₃ during the discharge and charge processes (Fig. S21), further corroborating the results of XRD and XPS analysis [9, 13]. In addition, the XRD and XPS spectra of fully discharged Ru/CNFs and Cu/CNFs cathode electrodes also display the formation of Li₂CO₃ products (Fig. S22 and Fig. S23). However, the peaks intensities of XRD and XPS corresponding to the Li₂CO₃ are merely slightly decreased for both the fully charged Ru/CNFs and Cu /CNFs cathode electrodes, indicating the limited capability of Ru/CNFs and Cu /CNFs electrocatalysts for effectively decomposing Li₂CO₃, which is consistent with their low Coulombic efficiency (Fig. 4d and Fig. S22).

The corresponding morphology changes of *i*-Ru₄Cu₁/CNFs electrodes after full discharge and charge were further examined by SEM and TEM. As shown in Fig. 5d and 5f, the discharged *i*-Ru₄Cu₁/CNFs electrode surface is totally covered by Li₂CO₃. We can deduced that the alloyed *i*-Ru₄Cu₁ nanoparticles with the downshifted d-band center facilitate generation and dispersion of Li₂CO₃. With increasing discharge depth, the discharge products gradually extend along CNFs surface and eventually cover whole electrode as well as *i*-Ru₄Cu₁ nanoparticles. Massive Li₂CO₃ would block contact between active sites and reactants, being the chief reason for degradation of battery performance. Notably, it can be seen from Fig. 5e and 5g that the Li₂CO₃ products fully disappear after recharging under the help of high-performance *i*-Ru₄Cu₁/CNFs, and the morphology of *i*-Ru₄Cu₁/CNFs electrode returns back to initial state, preparing for next discharge-charge cycle.

As mentioned in previous researches [9, 12], the reaction mechanism of Li-CO₂ batteries is proposed to be the reversible reaction of $4\text{Li} + 3\text{CO}_2 \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$. The Li₂CO₃ and C species are co-produced during the discharge process. While, during the charge process, only CO₂ gas is emitted through the reaction between Li₂CO₃ and C. Therefore, to well confirm the CO₂ gas emission and examine the discharge products during the cycling process in Li-CO₂

batteries, we have systematically carried out the gas chromatography (GC) and Raman measurements by using the carbon-free $i\text{-Ru}_4\text{Cu}_1$ nanomaterials in the customized Swagelok-type Li-CO₂ batteries (Fig. S24). As shown in Fig. 6a, the Li-CO₂ battery was firstly discharged to a capacity of 5000 mAh g⁻¹ at the current density of 300 mA g⁻¹ in the pure CO₂ gas. Subsequently, after introducing pure Ar gas into such discharged battery to completely eliminate the residual CO₂, such Li-CO₂ battery was recharged to 5000 mAh g⁻¹ for detecting the gas emission during the charge process [29, 64]. Accordingly, three different points (A, B and C) were sequentially taken from the charge process in Fig. 6a to monitor the gas emission by the gas chromatography (GC) instrument. It can be clearly seen that only CO₂ gas is detected over the charge process (Fig. 6b). Furthermore, the Raman spectroscopy of discharged carbon-free electrode clearly demonstrates the formation of Li₂CO₃ and C products. The peak at 1089 cm⁻¹ is ascribed to be Li₂CO₃, and the peaks emerging around 1348 cm⁻¹ and 1581 cm⁻¹ can be identified to be the D and G bands of the produced carbon species after discharge [12, 25]. Intriguingly, after charging such Li-CO₂ battery, the characteristic peaks of Li₂CO₃ and C disappear, indicating that the Li₂CO₃ and C species can be simultaneously decomposed during the charge process. Therefore, based on above comprehensive and fundamental characterizations of GC and Raman spectra, it can be evidently confirmed that the Li₂CO₃ and C species are the main discharge products in Li-CO₂ batteries, and such Li₂CO₃ and C species can be reversibly decomposed to release the only gas of CO₂ over the charge process. As a result, the reaction mechanism of Li-CO₂ batteries based on $i\text{-Ru}_4\text{Cu}_1$ electrocatalysts is identified to be the reversible reaction of $4\text{Li} + 3\text{CO}_2 \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$, which is in line with previous reports [9, 12]. Generally, for the practical Li-CO₂ batteries, the carbon nanomaterials, such as Ketjen black [12] and CNFs [15], are commonly employed as the substrates for dispersing the active metal nanoparticles and improving the conductivity. It is a possibility that the Li₂CO₃ may selectively react with the CNFs substrates during the charge process, which may be a potential factor for the

degradation of batteries performance. However, it is difficult to distinguish the produced carbon through the reaction of $4\text{Li} + 3\text{CO}_2 \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$ from the carbon substrates in the practical Li-CO₂ batteries, and currently, the specific reaction mechanism between C and Li₂CO₃ is complex and is still unclear. Hence, in the future, more efforts should be devoted on such fundamental investigations to clearly probe the corresponding reaction mechanism.

Conclusions

In summary, we for the first time report the intermixed bimetallic RuCu nanoalloys that uniformly dispersed on CNFs (*i*-Ru₄Cu₁/CNFs) as high-performance cathode electrocatalysts for highly reversible Li-CO₂ batteries. Owing to the optimized compositional and electronic effects, the *i*-Ru₄Cu₁/CNFs could effectively facilitate the formation and decomposition of Li₂CO₃ products during discharge and charge processes, showing exceptional electrocatalytic performance for Li-CO₂ batteries. The Li-CO₂ batteries based on *i*-Ru₄Cu₁/CNFs cathodes exhibit ultra-low overpotentials and can be steadily cycled for over 110 cycles at 500 mA g⁻¹ with a fixed capacity of 1000 mAh g⁻¹. Moreover, they show the record-high rate capability. These findings reveal that *i*-Ru₄Cu₁/CNFs is highly active and stable for Li-CO₂ battery performance, much superior to most reported electrocatalysts, which also provides novel view for developing more advanced cathodes in Li-CO₂ and other metal-air batteries.

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Figure captions

Fig. 1. (a) XRD patterns of Ru/CNFs and *i*-Ru₄Cu₁/CNFs. Inset in (a) is the corresponding enlarged image. (b, c) Bright-field TEM image of *i*-Ru₄Cu₁/CNFs. (d) HRTEM of *i*-Ru₄Cu₁/CNFs derived from the yellow frame in (c). (e) Lattice fringe distance for *i*-Ru₄Cu₁ nanoalloy derived from the blue frame in (d). (f) HAADF-STEM image and (g-i) corresponding element mappings. (j) Line-scan of a single *i*-Ru₄Cu₁ nanoparticle.

Fig. 2. (a) Full XPS survey spectra for Ru/CNFs, *i*-Ru₄Cu₁/CNFs and Cu/CNFs. (b) High-resolution XPS spectra of Ru3*p* for Ru/CNFs and *i*-Ru₄Cu₁/CNFs. (c) High-resolution XPS spectra of Cu2*p* for *i*-Ru₄Cu₁/CNFs and Cu/CNFs. (d) Valence band spectra (VBS) for Ru/CNFs, *i*-Ru₄Cu₁/CNFs and Cu/CNFs.

Fig. 3. (a) Galvanostatic discharge-charge curves of Li-CO₂ batteries based on *i*-Ru₄Cu₁/CNFs, Ru/CNFs and CNFs electrocatalysts at current density of 100 mA g⁻¹ with cut-off capacity of 1000 mAh g⁻¹. (b) Comparison of overpotentials, discharge and charge voltages derived from (a). (c) Galvanostatic discharge-charge curves of Li-CO₂, Li-O₂ and Li-air batteries based *i*-Ru₄Cu₁/CNFs electrocatalysts at current density of 100 mA g⁻¹ with cut-off capacity of 1000 mAh g⁻¹. (d) Cycling ability of Li-CO₂ batteries based on *i*-Ru₄Cu₁/CNFs and Ru/CNFs electrocatalysts at current density of 500 mA g⁻¹ with cut-off capacity of 1000 mAh g⁻¹. (e) Selected discharge-charge curves of Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs electrocatalyst. (f) Comparison of time-voltage curves during the whole discharge-charge processes.

Fig. 4. (a) Rate capabilities and (b) comparison of overpotentials of Li-CO₂ batteries based on *i*-Ru₄Cu₁/CNFs and Ru/CNFs electrocatalysts at current densities ranging from 100 mA g⁻¹ to 2000 mA g⁻¹. (c) Selected discharge-charge curves of Li-CO₂ battery based on *i*-Ru₄Cu₁/CNFs electrocatalyst at various current densities. (d) Full discharge-charge curves of Li-CO₂ batteries based on *i*-Ru₄Cu₁/CNFs and Ru/CNFs electrocatalysts at current density of 300 mA g⁻¹.

Fig. 5. (a) XRD patterns of discharged and charged *i*-Ru₄Cu₁/CNFs electrodes in Li-CO₂ batteries. High-resolution XPS spectra of (b) discharged and (c) charged *i*-Ru₄Cu₁/CNFs electrodes in Li-CO₂ batteries. SEM images of (d) discharged and (e) charged *i*-Ru₄Cu₁/CNFs electrodes in Li-CO₂ batteries. TEM images of (f) discharged and (g) charged *i*-Ru₄Cu₁/CNFs electrodes in Li-CO₂ batteries.

Fig. 6. (a) Galvanostatic discharge-charge profile of Li-CO₂ battery based on a carbon-free *i*-Ru₄Cu₁ cathode electrode at a current density of 300 mA g⁻¹ with cut-off capacity of 5000 mAh g⁻¹. (b) the GC curves of selective points during the charge process obtained from (a). (c) The Raman spectra of the discharged and charged carbon-free *i*-Ru₄Cu₁ cathode electrodes in the Li-CO₂ batteries at a current density of 300 mA g⁻¹ with cut-off capacity of 5000 mAh g⁻¹.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6