Supporting Information

Facile fabrication of Ni, Fe-doped δ -MnO₂ derived from Prussian blue

analogues as efficient catalyst for stable Li-CO₂ batteries

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Experimental Section

Materials: All reagents are of analytical grade and without further purification. Nickel(II) chloride hexahydrate (NiCl₂·6H₂O), trisodium citrate dihydrate, potassium ferrocyanide (K₃[Fe(CN)₆]), lithium bis(trifluoromethane sulfonimide) (LiTFSI), tetraethylene glycol dimethyl ether (TEGDME, tetraglyme) were purchased from Aladdin Biochemical Technology Co., Ltd. Potassium permanganate, potassium chloride and N-methyl-2-pyrrolidone (NMP) were brought from Sinopharm Chemical Reagent Co., Ltd. Commercial multiwall CNTs [diameter × length:(5-15 nm) × (10- 30 μ m), purity: >95%] were purchased from XFNANO, Inc. (Nanjing, China). Carbon paper (CeTech GDS180S) was obtained from the Toray Industries, Inc.

Preparation of Ni-Fe PBA: The material was prepared according to the previous literature.¹ In brief, 15 mmol NiCl₂·6H₂O and 22.5 mmol trisodium citrate dihydrate were dissolved in 500 mL deionized water to form solution A. 10 mmol of K_3 [Fe(CN)₆] was dissolved in 500 mL deionized water to form solution B. After then, solution A and solution B were mixed, stirred under magnetic stirring for 5 minutes to make them blend well, and then aged for one week at room temperature. The yellow precipitates were collected by centrifugation, washed for three times with deionized water and ethanol, respectively. Finally, the products were obtained after dryying in a vacuum oven at 70 °C.

Preparation of Ni-Fe-δ-MnO₂: Firstly, 0.1 g Ni-Fe PBA, 0.474 g KMnO₄ and 0.224 g KCl were dissolved in 35 mL deionized water in turn to form a homogeneously

transparent solution. After stirring for 20 min, the mixed solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and placed into an oven at 180 °C for 2 h. After the reaction, the brown precipitate was collected by centrifugation, washed for several times with deionized water and anhydrous ethanol, and dried in a vacuum oven at 70 °C, denoted as Fe- δ -MnO₂ precursor. Finally, the Fe- δ -MnO₂ precursor was placed in a tube furnace under Ar gas atmosphere and calcined at 300 °C for 2 h with a heating rate of 2 °C/min to obtain Ni-Fe- δ -MnO₂. The synthetic process of δ -MnO₂ is the same as that of Ni-Fe- δ -MnO₂ except that Ni-Fe PBA is not added.

Materials characterization: The micromorphology of the samples was observed by field-emission scanning electronic microscopy (FE-SEM; TESCAN MIRA LMS). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were collected on a FEI Talos F200X electron microscope. X-ray diffraction (XRD) was recorded using 3kW D/MAX2200V Rigaku Cu. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Scientific K-Alpha X-ray photoelectron spectroscopy. The Brunauer-Emmett-Teller (BET) surface area were determined by nitrogen-desorption with Micromeritics ASAP 2460. Fourier transform infrared (FTIR) spectra were collected on Thermo Scientific IN10. Raman spectroscopy was performed on Renish in plus with the excitation wavelength: of 532 nm.

Battery assembling and electrochemical characterizations: Li-CO₂ batteries were assembled with a classical CR2032-type coin cells and conducted in an Ar-filled glove box with high-purity argon ($O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm). For the cathode

preparation, Ni-Fe- δ -MnO₂ or δ -MnO₂, CNT and PVDF were mixed at a mass ratio of 45 : 45 : 10 with N-methyl-2-pyrrolidinone as the solvent. The slurry was uniformly coated on carbon paper and then dried in an oven at 80 °C for 12 h. Li-CO₂ cells were assembled with 1 mol L⁻¹ LiTFSI in TEGDME as the electrolytes, a Li foil as anode, and Whatman glass fiber as the separator. The as-assembled battery was loaded into a homemade bottle filled with high purity CO₂ and stabilized for 8 h before electrochemical measurements. The galvanostatic charge and discharge processes were tested on LAND-CT2001. Cyclic voltammetry (CV) tests were carried out on the CHI760D electrochemical workstation at a scan rate of 0.1 mV/s in the voltage range of 2.0-4.5 V.



Fig. S1 (a) XRD pattern of Ni-Fe-PBA. (b) SEM image of Ni-Fe-PBA. (c, d) Initial morphology of Ni-Fe-PBA after hydrothermal etching.



Fig. S2 N_2 adsorption-desorption isotherms (a) and corresponding pore size distribution of Ni-Fe- δ -MnO₂.



Fig. S3 (a) Cyclic voltammetry (CV) curves of Li-CO₂ batteries with Ni-Fe- δ -MnO₂ under different atmospheres. (b) Full discharge–charge curves of Ni-Fe- δ -MnO₂ and δ -MnO₂ cathode for Li-CO₂ batteries at a current density of 100 mA g⁻¹.



Fig. S4 Discharge and charge curves of the Ni-Fe PBA cathode at a current density 100 mA g^{-1} in Li-CO₂ batteries.



Fig. S5 Rate performance of Ni-Fe- δ -MnO₂ cathode.



Fig. S6 SEM images of the Ni-Fe-δ-MnO₂ electrode at different stages: (a) discharged,(b) recharged.

Elements	Ni (wt%)	Fe (wt%)	Mn (wt%)	K (wt%)
Content	7.57	4.22	58.82	8.75

Table S1 The element content of Ni, Fe, K and Mn in the Ni-Fe- δ -MnO₂ from ICP-MS results.

References

1 H. Liao, X. Guo, Y. Hou, H. Liang, Z. Zhou, H. Yang, Small 2020, 16, 1905223.