Electronic Supplementary Information

Robust fluorite-structured high-entropy oxides with integrated multi-active site construction for Li-CO_2 batteries catalytic cathodes

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1. Materials characterization

1.1 Materials and Reagents. All the reagents were analytic grade and used as purchased without further purification. Cerium acetate ($(CH_3CO_2)_3Ce{\cdot}xH_2O$), iron chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), nickel acetate tetrahydrate ($NiC_4H_6O_4{\cdot}4H_2O$), Cobalt (II) acetate tetrahydrate ($C_4H_6CoO_4{\cdot}4H_2O$), manganese acetate tetrahydrate ($MnC_4H_6O_4{\cdot}4H_2O$), 1,3,5-Benzenetricarboxylic acid (BTC), cetyltrimethylammonium bromide (CTAB), $LiCF_3SO_3$, tetraethylene glycol dimethyl ether (TEDGME), N-Methylpyrrolidone (NMP), methanol and imidazole were bought from Macklin Biochemical Co., Ltd. Ultrapure water was used in all experiments.

1.2 Material preparation. The target samples were prepared by a facile MOFs precursor method. Specifically, 1 mmol of $(CH_3CO_2)_3Ce{\cdot}xH_2O$ and 0.25 mmol of $FeCl_3{\cdot}6H_2O$, $NiC_4H_6O_4{\cdot}4H_2O$, $C_4H_6CoO_4{\cdot}4H_2O$ and $MnC_4H_6O_4{\cdot}4H_2O$ were first dissolved in 50 mL of water to form solution A. Subsequently, 30 mg of CTAB and 2.5 mmol of BTC were dissolved in 50 mL of water to form solution B. The solution A was added drop by drop to B under stirring at room temperature for 1.5 h. Then, the samples were centrifuged and washed with water and ethanol to remove impurities. The prepared precursor was soaked in methanol overnight and then dried in a vacuum drying oven. The dried precursor was ball-milling for 24 h and heated up to 500℃ at a rate of 1℃/min and kept for 2 h. After natural cooling, the target product fluorite-type high entropy oxides $(CeFeCoNiMn)O_x$ (labeled as HEOs) was obtained. As comparison, CeO_2 and $(FeCoNiMn)O_x$ (labeled as TOs) were obtained by leaving out the addition of Ce source or by leaving out the addition of Fe/Co/Ni/Mn species and by going through the same preparative process.

1.3 Materials Characterization. The physical structure of the samples was examined using X-ray diffraction (XRD) patterns generated by Cu Kα radiation (λ = 1.541 Å) on a Bruker D8 diffractometer. Raman spectra were acquired within the range of 0 to 800 cm^{-1} using a LabRAM HR spectrometer. To analyze the surface electronic states, X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific ESCALAB 250Xi instrument, employing C 1s (284.8 eV) for calibration. Morphological and surface visualizations were enhanced through the use

of transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) on a JEM-2010 system. Fourier Transform Infrared (FTIR) spectra were recorded using a NEXUS 470 spectrophotometer with a KBr base. Additionally, nitrogen adsorption/desorption isotherms were determined using an ASAP 2460 analyzer for specific surface area and porosity assessments.

1.4 Li-CO_2 batteries assembly. Preparation of cathode sheets is essential for Li-CO_2 batteries prior to assembly. Initially, a catalyst ink was formulated by mixing the active material, binder (PVP), and conductive agent (Super P) in NMP solvent at a 8:1:1 mass ratio. This ink was then coated onto carbon paper and dried at 60°C. Subsequently, the coated paper was cut into 14 mm diameter discs to form the catalytic cathodes, with an active material mass density of approximately 0.35 mg cm^{-2} on the paper. A CR2032 cell was assembled for the Li-CO_2 battery, featuring a cathode side with a hole, a 16 mm diameter lithium metal anode, an 18 mm diameter glass fiber separator, and 70 μL of 1M $LiCF_3SO_3$ in TEGDME as the electrolyte. Post-assembly, the cells were placed in a sealed box filled with CO_2 and allowed to equilibrate at 25°C for 12 hours. Battery testing was conducted using a LAND CT 3001A tester in either voltage-limit mode (ranging from 2.0 to 4.5 V at 100 mA g^{-1}) or capacity-limit mode (1000 mA h g^{-1} at 100 mA g^{-1}). The measurements account for current density and specific capacity based on the active material's quantity. Additionally, electrochemical impedance spectroscopy (EIS) was performed over a frequency range of 1 MHz to 1 mHz with a 5 mV amplitude, and cyclic voltammetry (CV) is conducted within 2.0 to 4.5 V at a scan rate of 0.1 mV s^{-1}, both using a CHI 760E workstation.

Table S1. The ICP-MS measurement results of the synthesized $CeFeCoNiMnO_x$.

sample	$CeFeCoNiMnO_x$
Ce / mass ratio	56.2%
Fe / mass ratio	5.1%
Co / mass ratio	4.8%
Ni / mass ratio	5.0%
Mn / mass ratio	4.5%

Based on the calculation of the results of the ICP-MS test it can be measured that the atomic ratios of Ce, Fe, Co, Ni, Mn, and O in the $CeFeCoNiMnO_x$ samples are 17.7%, 4.0%, 3.6%, 3.8%, 3.6%, and 67.4%, respectively.

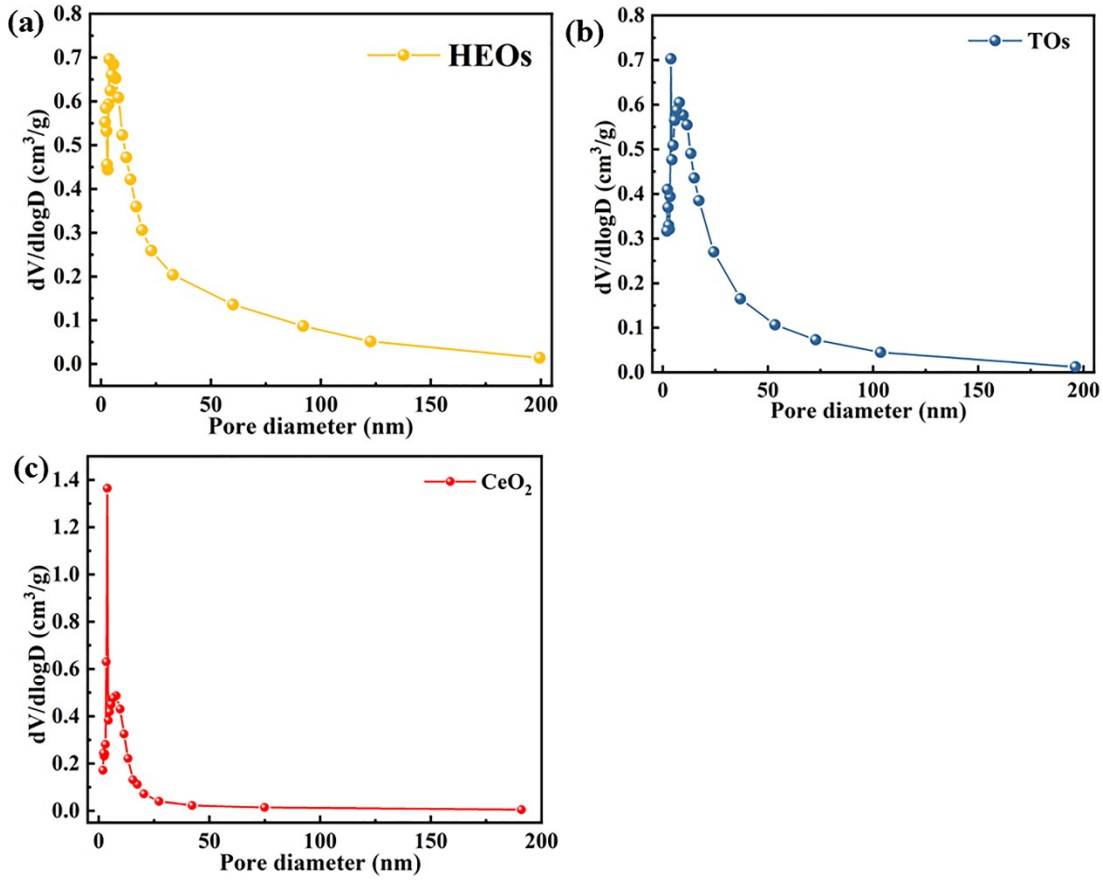

Fig. S1. (a-c) Pore size distribution of prepared samples.

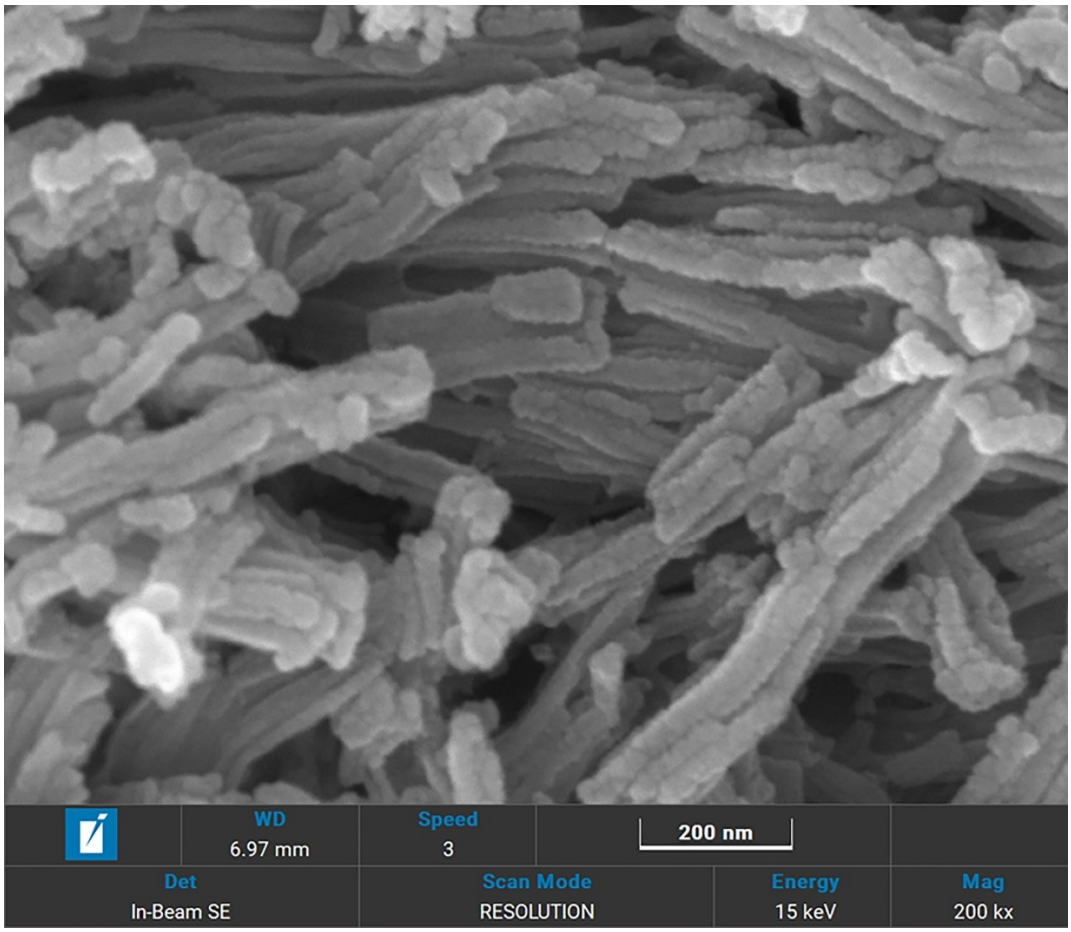

Fig. S2. SEM image of HEOs.

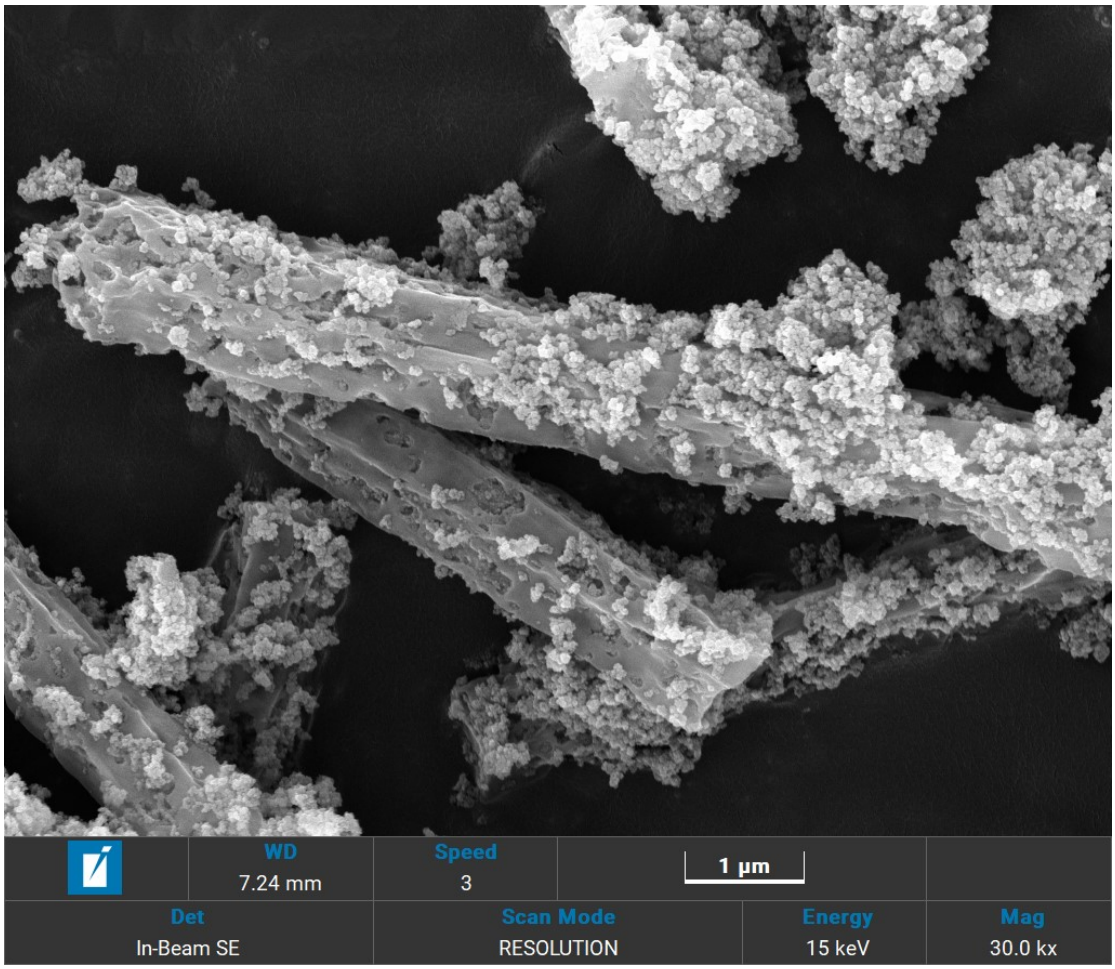

Fig. S3. SEM image of TOs.

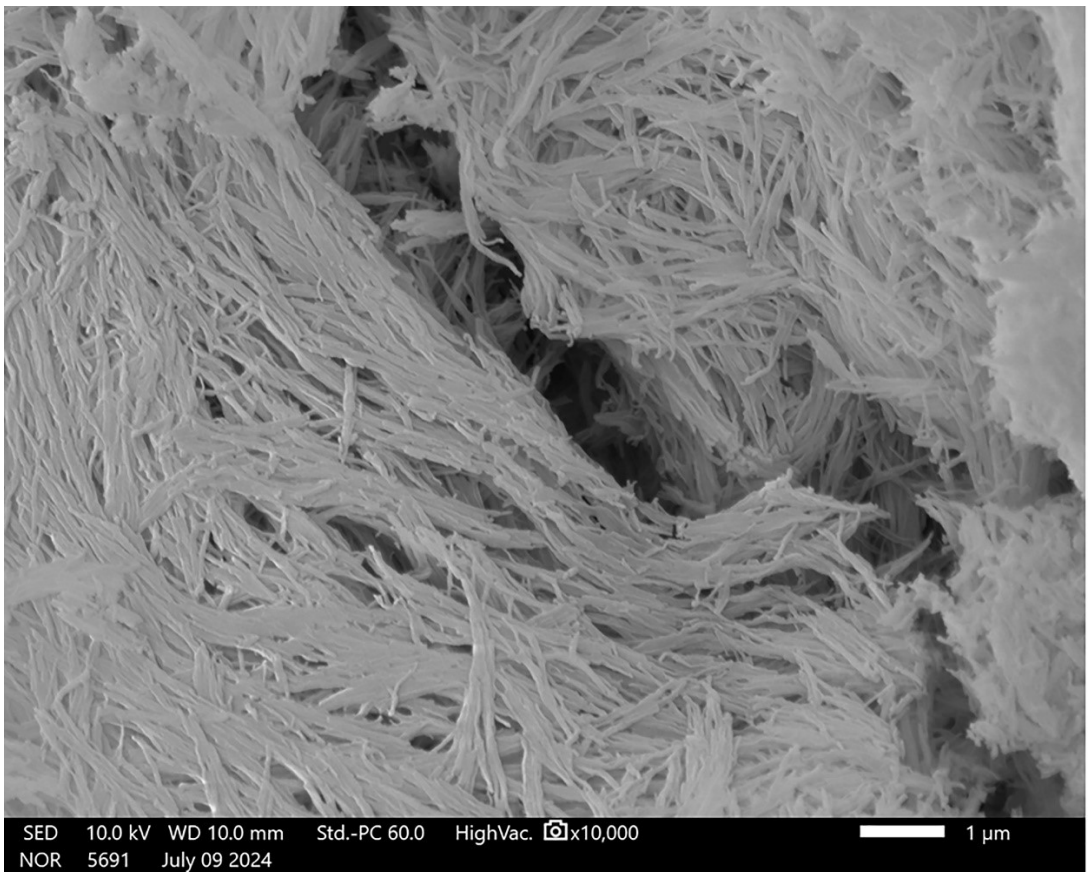

Fig. S4. SEM image of CeO_2.

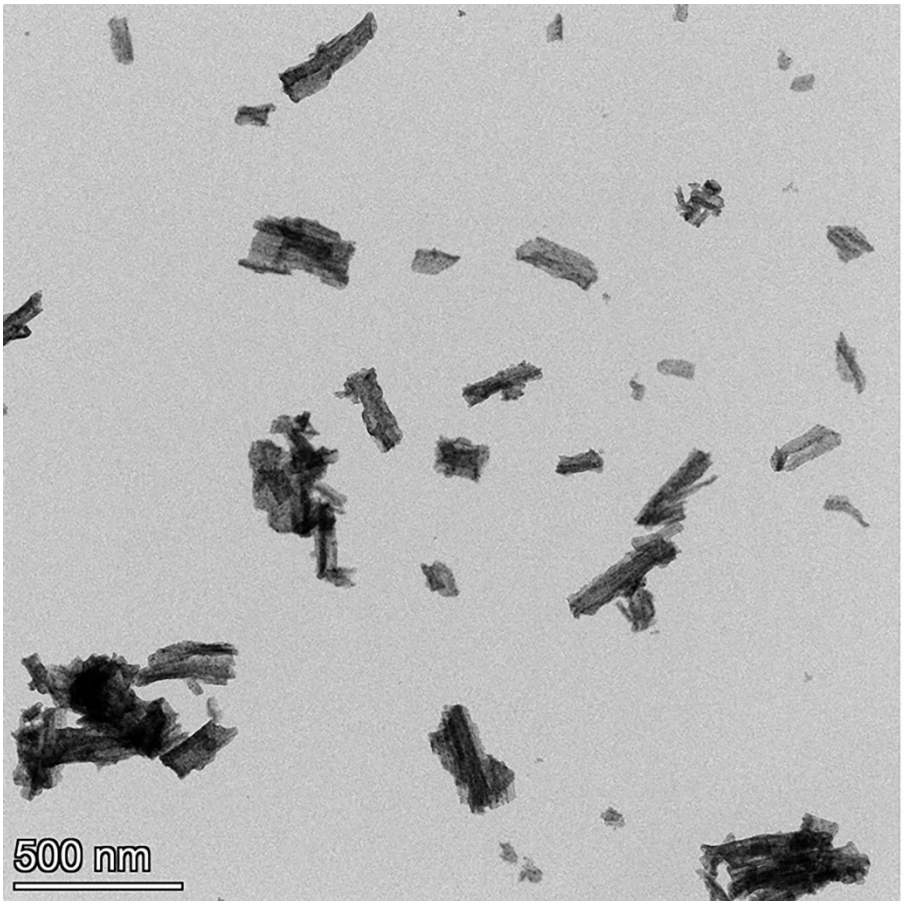

Fig. S5. TEM image of HEOs.

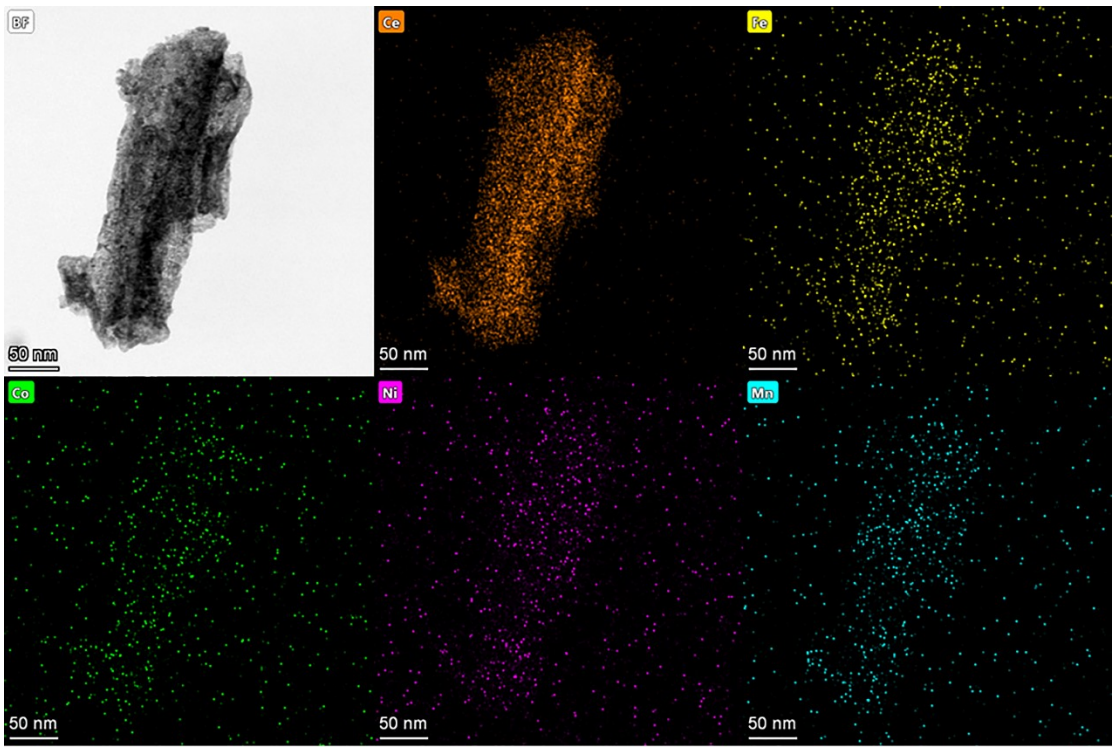

Fig. S6. The TEM image and EDS mapping of the corresponding element in HEOs.

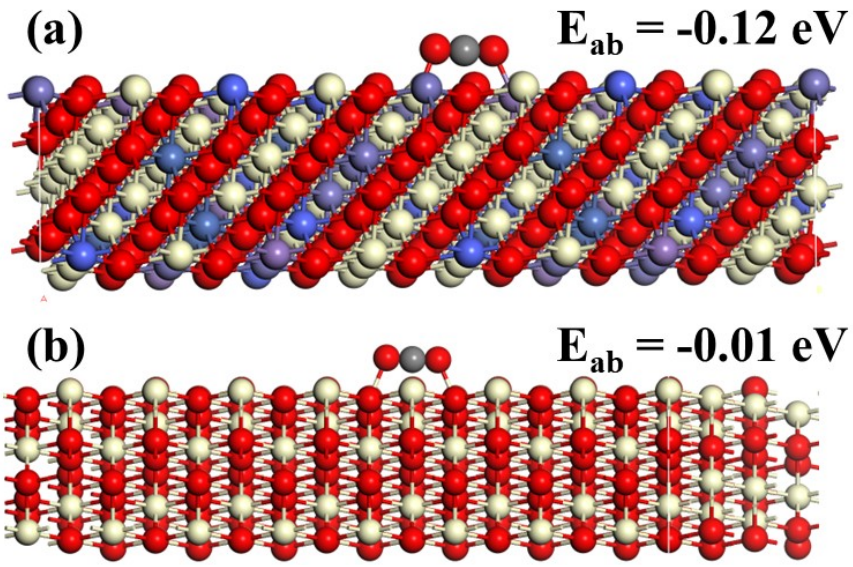

Fig. S7. The adsorption model diagram of each component in the catalytic cathode for CO_2 molecule. (a) CO_2 molecules adsorbed on $CeFeCoNiMnO_x$. (b) CO_2 molecules adsorbed on CeO_2.

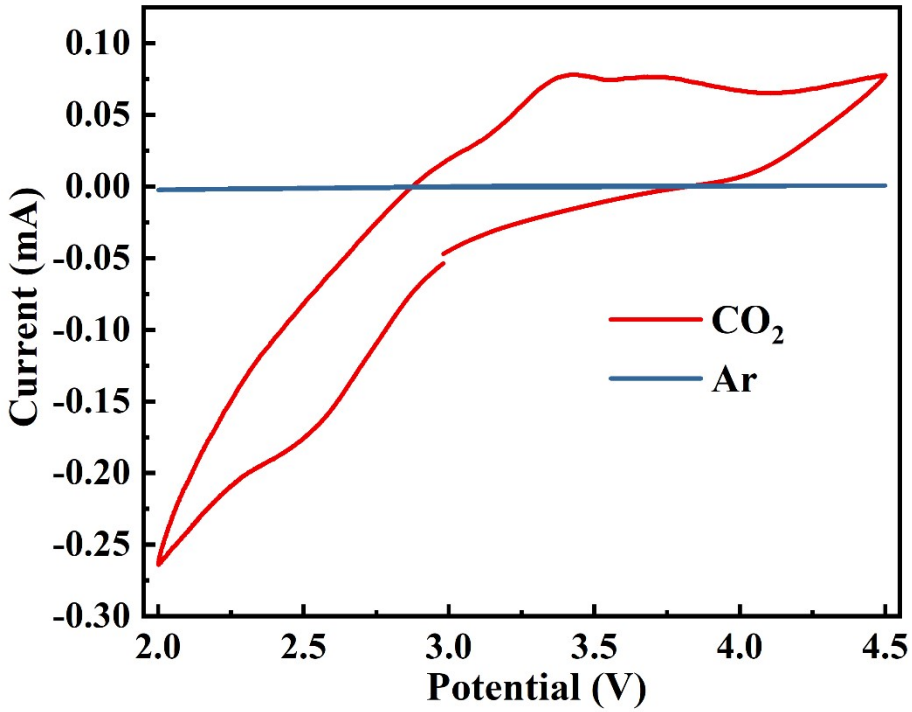

Fig. S8. Cyclic voltammetry for HEOs based Li-CO_2 batteries at different atmosphere.