Electronic Supplementary Information

Hierarchical hollow nanofiber networks for high-performance hybrid direct carbon fuel cells

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Experimental

Preparation of CMF nanofiber

The CMF nanofibers were prepared by electrospinning method. First, polyvinylpyrrolidone (PVP, 8 wt%) were dissolved into 7.5 mL N, N- dimethylformamide (DMF) at room temperature under stirring until a clear solution was formed. And then, stoichiometric amounts of $Ce(NO3)_3 \cdot 6H_2O$,$Mn((NO3)_2 \cdot 4H_2O$ and $Fe(NO3)_2 \cdot 9H_2O$ with a molar ratios of 0.6:0.3:0.1 were added into the above solution until complete dissolution. Afterwards, the final solution was loaded into a plastic syringe equipped with a stainless needle of 0.81mm in diameter. A syringe pump was used to pump the solution at a high electric field of 1.0 $kV \cdot cm^{-1}$ and CMF/PVP precursors were collected on aluminum foil simultaneously. Then, CMF nanofibers were achieved after the CMF/PVP precursors being calcined for 2 h at 800 °C in air.

Fabrication of single cells

The electrolyte-supported single cell with the cell configuration of CMF/ $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) / $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) was prepared. Dense LSGM electrolyte disc was prepared by uniaxially pressing 0.5 g LSGM powder into pellets, and then sintered at 1450 °C for 6 h in air with a diameter of 15 mm. The LSCF cathode slurry was coated

onto one side of LSGM electrolyte surface, and then calcined at 1100 °C for 2h to serve as cathode. The CMF nanofibers were mixed with 3 wt% ethyl-cellulose terpinol solution to form anode slurry. The anode slurry was pasted on other side of LSGM electrolyte surface, and then heated at 850 °C for 2 h in air. The active area of as-prepared anode was 0.36 cm^2. Finally, Ag paste was printed onto the electrode and sintered at 750 °C for 30 min to collect current.

To infiltrate Ni into the CMF nanofiber anode, a precursor solution was prepared by dissolving 0.25M $Ni(NO_3)_2 \cdot 6H_2O$ into deionized water. The precursor solution was infiltrated into CMF nanofiber anode scaffold (weight ratio of NiO to CMF is 30:70), and sintered at 450 °C for 30 min to form the infiltrated CMF-NiO composite anode. The infiltration amount is defined as the amount of NiO divided by the total amount of CMF-NiO composite anode, where the amount of NiO is equal to subtract the amount of bare CMF h-NF anode from the total amount of CMF-NiO composite anode. And both of the amounts of bare CMF h-NF anode and CMF-NiO composite anode are weighted by the electronic balance.

Structural and electrochemical characteristics

The crystalline structure of as-prepared CMF nanofibers and the phases in CMF-30NiO anode on LSGM electrolyte were determined by X-ray diffraction (XRD) (X' Pert PRO MPD) using Cu Kα radiation. Field scanning electron microscopy (SEM, FEI QUANTA-250) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) was carried out to monitor the morphology of as-prepared CMF hollow nanofibers. N_2 adsorption-desorption isotherm was determined by BET measurements using Autosorb-IQ2-MP-C surface area analyzer. The microstructures of single nanofiber after infiltration were characterized by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM, JEOL 2010F) equipped with Energy Dispersive Spectrometer (EDS).

In addition, the cell performance was measured using an Arbin Instruments' tester (Fuel Cell Test System, FCTS) with activated carbon as fuel. Before testing, lithium carbonate (Li_2CO_3) and potassium carbonate (K_2CO_3) (Aladdin, China) was mixed in a molar ratio of 62:38 by ball milling for 24 h and then used as the redox media in the cell device. Afterwards, 2 g of activated carbon and eutectic carbonate mixture (mass ratio of 4:1) was filled into the anode chamber, where argon gas (10 mL min^{-1}) was fed to prevent combustion of carbon fuel, and the cathode was

exposed to ambient air. The electrochemical resistance were measured under open circuit conditions by electrochemical impedance spectroscopy (EIS, PARSTAT 2273, USA), using a 10 mV DC signal in the frequency range of 10 mHz-100 kHz. The impedance data was fitted and with equivalent circuit LR (QR) (QR) by using ZsimpWin software, in which R represented a resistance and Q represented a constant phase element.

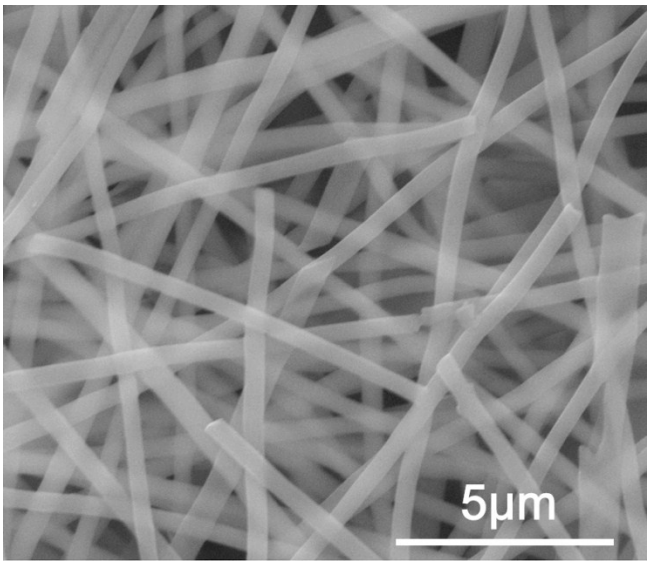

Fig. S1 SEM image of as-electrospun CMF/PVP nanofiber precursor.

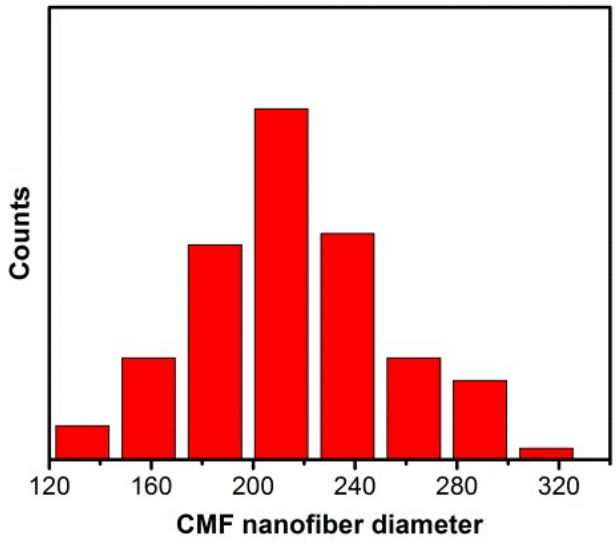

Fig. S2 Diameter distribution of the CMF hollow nanofibers.

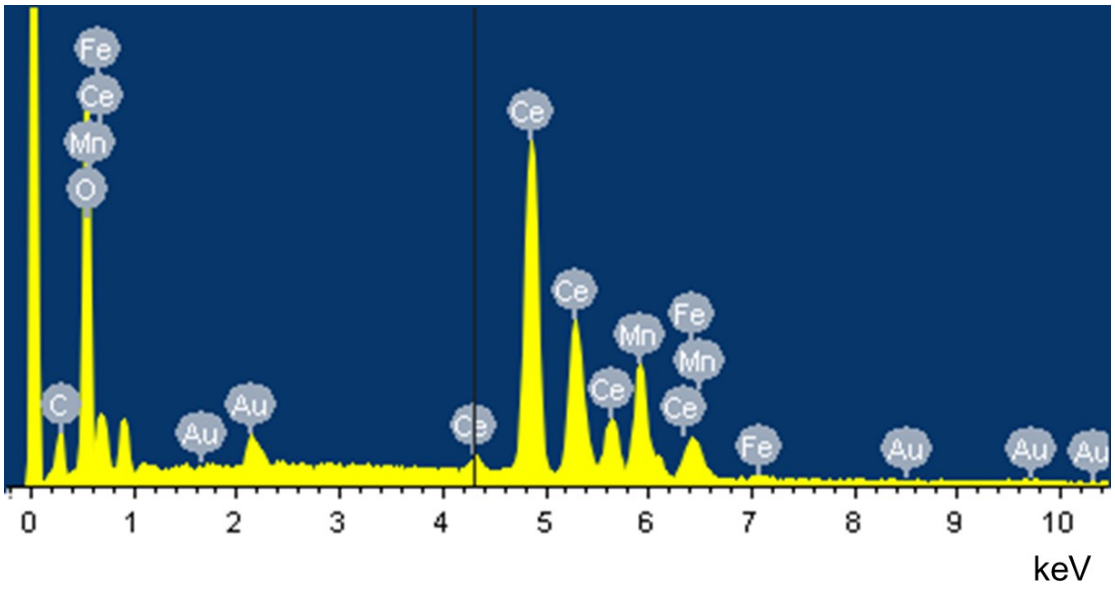

Fig. S3 EDX spectrum of the CMF hollow nanofibers.

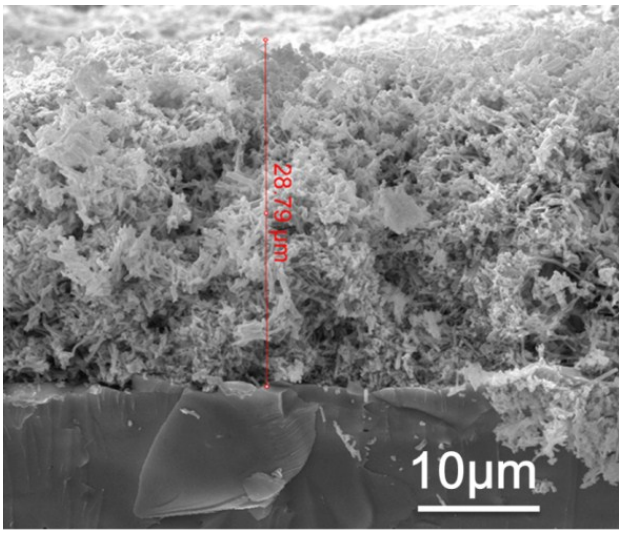

Fig. S4 SEM image shows the thickness of CMF h-NFs anode on LSGM electrolyte.

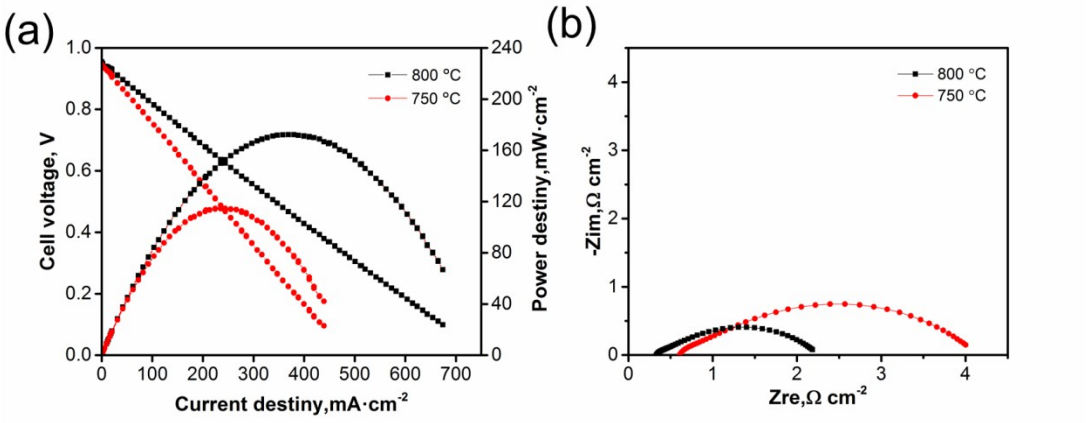

Fig. S5 Electrochemical performance of HDCFC with CMF nanoparticle anode in Ar tested at 800 and 750 °C. (a) *I-V*-P curves; (b) Impedance spectra testing under OCV conditions.

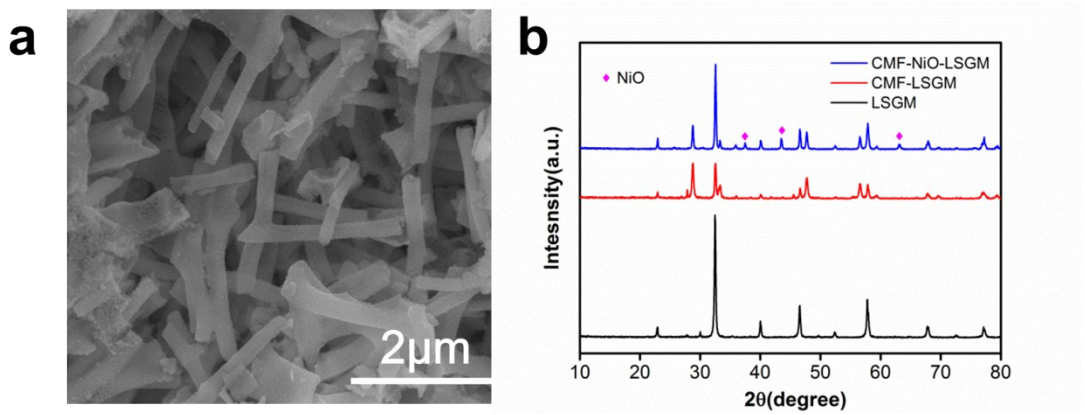

Fig. S6 (a) surface SEM images of Ni infiltrated CMF h-NF composite anode; (b) XRD patterns of LSGM electrolyte, CMF h-NF anode on LSGM electrolyte and Ni infiltrated CMF h-NF composite anode on LSGM electrolyte.

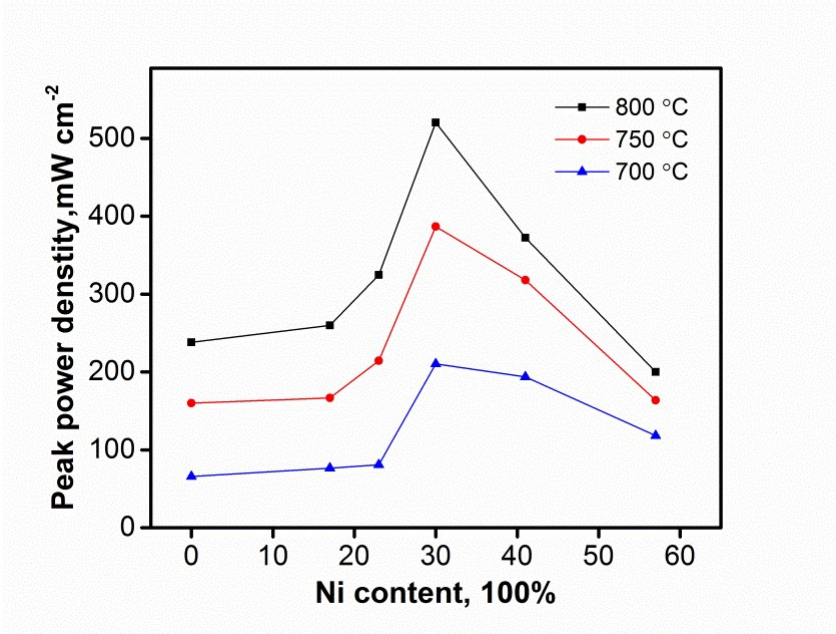

Fig. S7 Peak power densities of the single cells with different amounts of NiO tested at 700-800 °C.

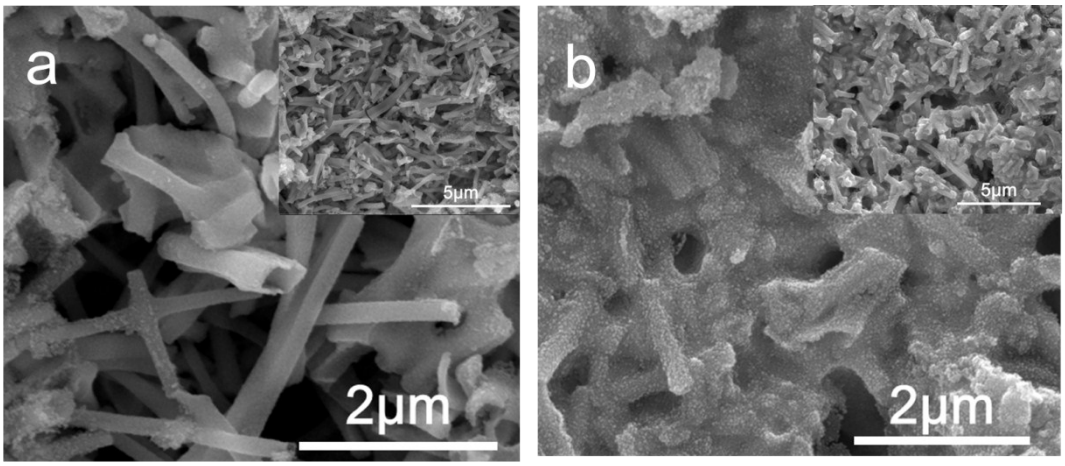

Fig. S8 SEM images of the Ni-infiltrated CMF nanofiber anode: (a) 30% NiO and (b) 57% NiO at low and high magnification

It has been reported that the infiltration amount is also a critical impact factor for the cell performance. Therefore, the electrochemical performance of HDCFCs with different amounts of infiltrated NiO is further evaluated in this communication. The anode in different mass fraction of x% NiO is prepared using the same procedure as Section 2.2, which is denoted in the following as CMF-xNiO (x=17, 23, 30, 41 and 57). Fig. S7 shows the maximum power densities of the cells with infiltrated CMF-xNiO anode measured at 700-800 °C. After infiltration, the MPD increases dramatically and it reaches the highest when 30% NiO is infiltrated into the electrode. However, further increase in the amount of NiO results in the deterioration in cell performance. To clarify the difference in cell performance with different amounts of infiltrated NiO, the microstructures of the infiltrated CMF-30NiO and CMF-57NiO anode are examined (Fig. S8). It can be observed that the porous hollow nanofiber structure is still remained after 30% NiO infiltrated (Fig. S8a). And adding moderate amount of NiO into CMF h-NF anode effectively improves the conductivity and catalytic activity. Therefore, the infiltrated CMF-30NiO composite anode exhibits higher power density. In contrast, after addition of 57% NiO into CMF h-NF anode, the anode porosity turns lower (Fig. S8b). The overloaded NiO blocks the gas transportation, and thus decreases the performance.