Supporting Information

Enhanced Stability and Catalytic Activity on Layered Perovskite Anode for High-Performance Hybrid Direct Carbon Fuel Cells

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1. Supporting figures

**Figure S1.** SEM images of (PrBa)$_{0.95}$Fe$_{1.8-x}$Cu$_x$Nb$_{0.2}$O$_{5+\delta}$ (PBFCN) powders at (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$, (d) $x = 0.4$.

**Figure S2.** The XRD patterns of as-prepared and reduced (PrBa)$_{0.95}$Fe$_{1.6}$Cu$_{0.4}$O$_{5+\delta}$, there is a secondary phase after the reduction at 800 °C.
Figure S3. (a) The I–V–P curves of the HDCFC with PBFCu₀.₄N anode that tested at 700–800 °C and (b) the corresponding impedance spectra testing under OCV conditions.

Figure S4. The I–V–P curves of the single cell before and after the stability test.
Figure S5. (a) The model and (b) physical maps of the bowl-shaped HDCFC.

Figure S6. HDCFC power generation unit: (a) As-prepared bowl-shaped YSZ electrolyte; (b) The cell after spraying the electrode.
Figure S7. Electrochemical performance of the SOFC with PBFCu$_{0.4}$N anode tested at 700–800 °C, 50ml min$^{-1}$ H$_2$ was introduced into the anode chamber as the fuel: (a) I–V–P curves and (b) impedance spectra testing under OCV conditions. The open circuit voltage (OCV) is close to the theoretical voltage calculated by Nernst equation, which is 1.182 V at 800 °C, 1.197 V at 750 °C, and 1.203 V at 700 °C, respectively, which means nice catalytic activity of PBFCu$_{0.4}$N. The maximum power density of the cell reaches 600.8, 359.5, 202.4 mW cm$^{-2}$ at 800, 750, and 700 °C, respectively.
Figure S8. TGA analysis of the fuel (mixture of the activated carbon and carbonate with a mass ratio of 4:1) in Ar, the weight loss before 100 °C is due to the loss of adsorbed water. When the test temperature reaches 800 °C, more than 20% of the weight loss indicates the occurrence of carbonate decomposition and reverse Boudouard reaction, so there will be enough CO in the anode chamber at the test temperature of 700–800 °C.
Figure S9. The microstructure of the PBFCu$_{0.4}$N anode after the discharge test that fueled by H$_2$. There is no in situ exsolved metal nanoparticles on the surface of anode, which proves the structure stability of PBFCN.

Figure S10. CO–TPD analyses of PBFCu$_{0.4}$N and PBFCu$_{0.5}$N, the appearance of CuO in PBFCu$_{0.5}$N changes the tendency of the desorption curve, but the chemical adsorption capacity of CO does not change significantly.
Figure S11. SEM image of the activated carbon used in this paper.