Supporting Information

Improving Electrochemical Properties of Carbon Paper as Cathodes for Microfluidic Fuel Cells by the Electrochemical Activation in Different Solutions

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*S*1 Detailed assembly steps of our MFC

The detailed assembly steps of our MFC are shown as below: First, the carbon paper electrode (1.5 mm ×15 mm) was placed in each electrode channel. Then the carbon paper (the 5 mm long front end) and the titanium foil (0.25 mm in thickness) were attached by double-sided carbon conductive adhesive (Japan). Here, the titanium foil was used as the current collector. Finally, the two PDMS plates and a silicone gasket (0.2 mm in thickness) were fastened by six 3 mm bolts (not shown). And the four 3 mm silicone tube were put in the four 3 mm holes in the upper plate as the inlets and outlets of the solution, respectively.

*S*2 FTIR Analysis

Further structural insights were obtained in FTIR measurements. From Figure *S*1, the samples of CP, CP-Na_2SO_4, CP-NaOH, and CP-H_2SO_4 can be seen to display five vibrational peaks, 3440 cm^{-1} due to the stretching of hydroxyl (-OH) groups, [1] 1590 cm^{-1} to the stretching of carbonyl (C=O) groups, [2,3] 1632 cm^{-1} to the C=C stretch of aromatic rings, [3,4] 1390 cm^{-1} to the curving vibration of alkyl C-H,[5] and 1100 cm^{-1} to the C-O stretch of ether groups.[5]
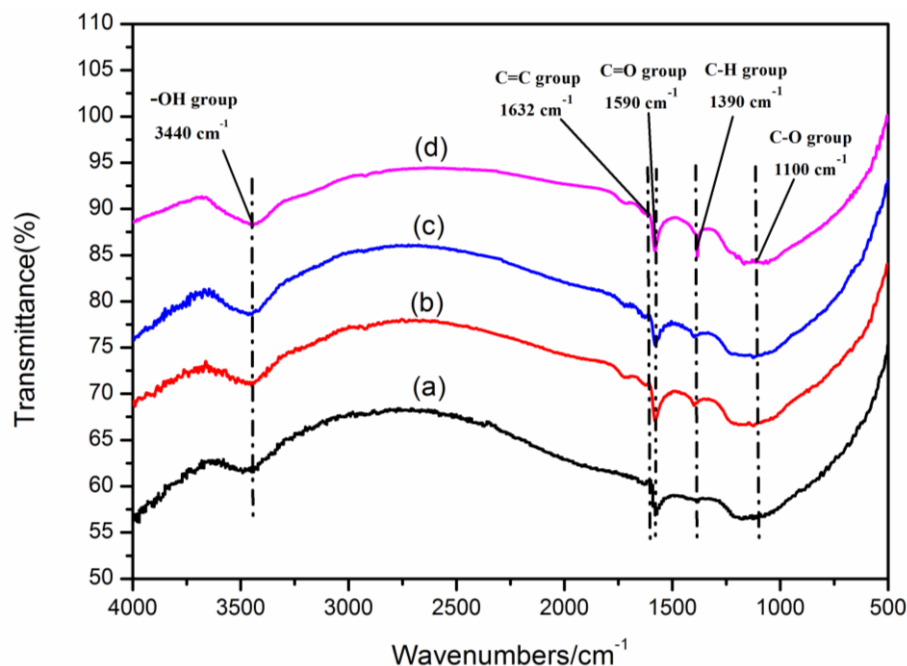
Figure *S*1 FTIR spectra curves of the four cathodes:

(a) CP, (b) CP-Na$_2$SO$_4$, (c) CP-NaOH, (d) CP-H$_2$SO$_4$.

*S*3 Contact angel experiment for the four samples

The contact angle of the CP is about 110.0°, shown in Figure *S*2. As the hydrophilicity of the other three electrodes is very high, the static contact angle experiments for these samples are not successful. The videos to record the contact angle experiments for the CP-Na$_2$SO$_4$, CP-NaOH and CP-H$_2$SO$_4$ electrode are provided as Video *S*1, *S*2 and *S*3 in the Supporting Information, respectively.

Based on these figures and videos, it is clear that the hydrophilicity of the carbon fiber paper has been improved after the electrochemical treatment.

CA left: 110.5?
CA right: 110.6?
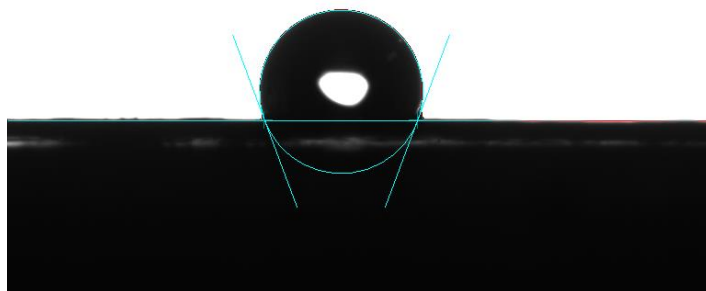
Figure *S*2 Cross-sectional view of water droplets on the carbon fiber paper of the CP electrode

*S*4 Electrochemical active surface areas for the four samples by CV measurements

We carried out CV measurements at different scanning rates to quantitatively gain the electrochemical active surface areas (EASA). The electrochemical active surface areas (EASAs) of the different cathodes by the CV tests were evaluated according to the equation below [6, 7]:

$$i_p = 2.69 \times 10^5 \, n^{3/2} \, (EASA) \, D_0^{1/2} \, C_0 v^{1/2}$$

where i_p is peak current (A), n is electron transfer number in the reduction reaction of $Fe(CN)_6^{3-}$ ($n=1$), EASA is electrochemical active surface area (cm^2), D_0 is the diffusion coefficient of $Fe(CN)_6^{3-}$ ($D_0=0.7\times10^{-5}$ cm^2 s^{-1}) [8], C_0 is $Fe(CN)_6^{3-}$ concentration ($C_0=5\times10^{-6}$ mol mL^{-1}), v is the scan rate (V s^{-1}).

Figure *S*3 depicts the CV curves of the four different electrodes under various scan rates (2-8 mV s^{-1}) in 0.1 M $LiClO_4$ as supporting electrolyte containing 5 mM $K_3Fe(CN)_6$. The EASA is calculated from the linear relationship between the cathodic or anodic peak currents and the square root of the scan rates.
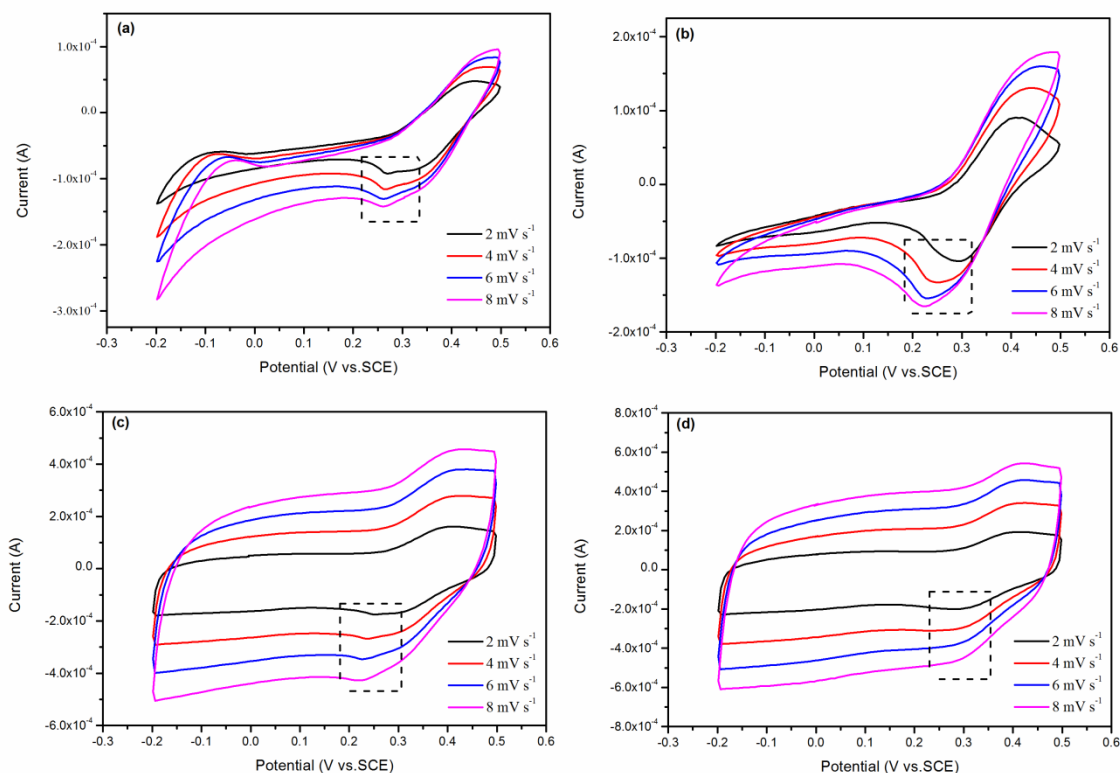
Figure *S*3 CV curves at various scan rates tested in 0.1 M LiClO$_4$ containing 5 mM K$_3$Fe(CN)$_6$ for the four electrodes: (a) CP, (b) CP-Na$_2$SO$_4$, (c) CP-NaOH, (d) CP-H$_2$SO$_4$. The dashed boxes highlight the cathodic peaks chosen for the calculation of the EASAs.

*S*5 Details of how to calculate the active electrode volume in Table 4

Table 4. Note: In ref. 28, the electrode volume was recalculated by multiplying the electrode surface (81.71 cm^2) area by the channel height (0.01 cm); in ref. 23, the volumetric density was calculated based on the active electrode volume (0.0027 cm^3); in ref.24, the size of the anode were 15mm $\times$ 3mm$\times$0.5mm. These data were used to calculate the effective reaction volume (0.00225 cm^3); in ref. 52, the cell performance was recalculated based on the anode volumes (0.3 cm$\times$1.0 cm$\times$0.18 cm=0.0054 cm^3); in ref. 26, the volumetric current density and power density were also calculated based the active electrode volumes (0.1 cm$\times$1.2 cm$\times$0.03 cm=0.0036 cm^3); in ref. 25, the reported current density and power density were normalized to the active electrode volume (0.05 cm$\times$1.0

cm$\times$0.07 cm=0.0035 cm^3).

Reference:

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