

## Supporting Information

### A robust esterified nanofibre electrode for proton exchange membrane fuel cells

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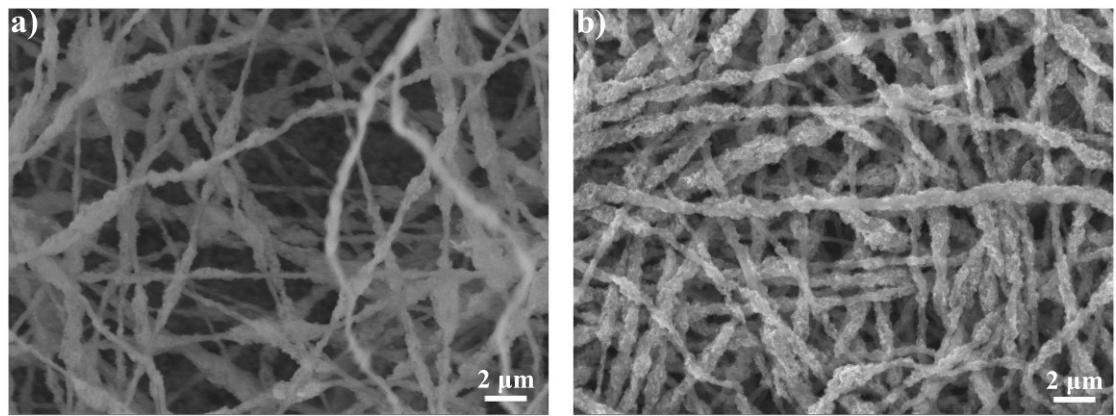
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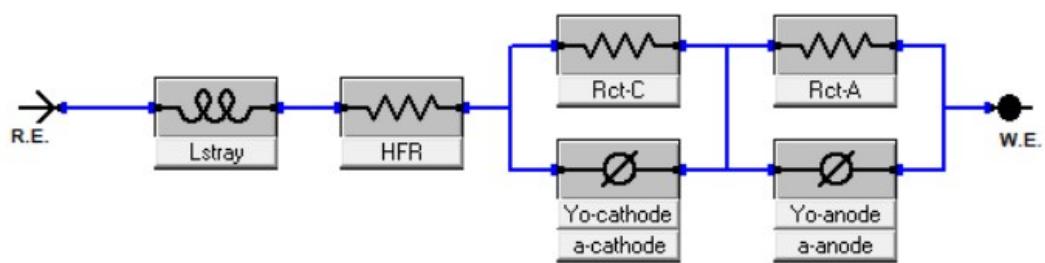
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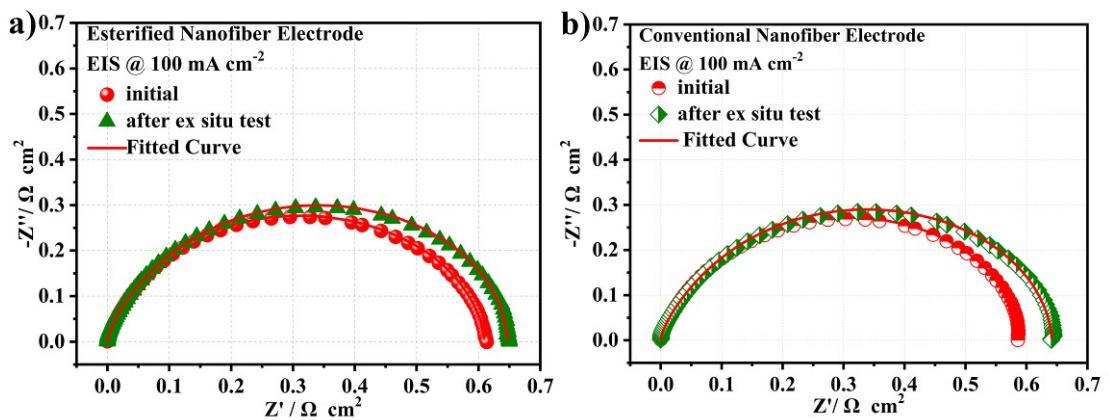
Fax: +86-411-84379185; Tel: +86-411-84379051, +86-411-84379153.



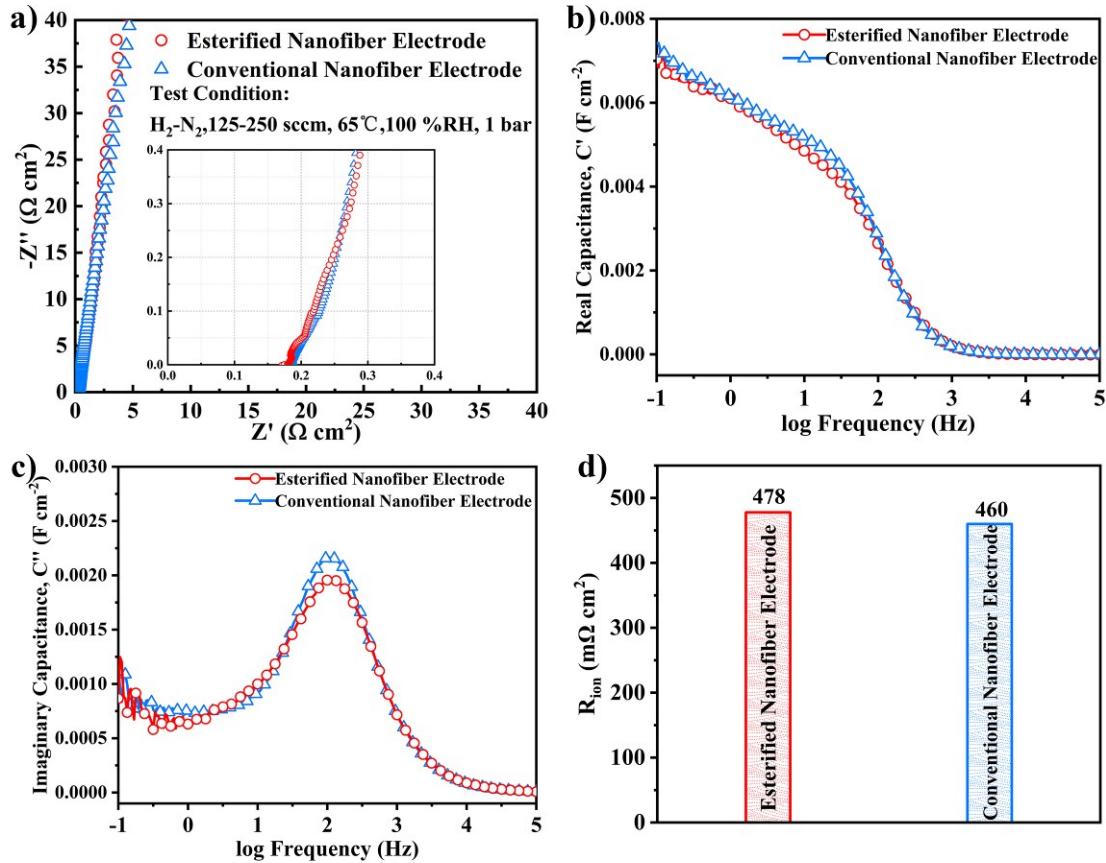
**Fig. S1.** The SEM images of the nanofibre electrode a) before and b) after the decal process.



**Fig. S2.** The equivalent circuit modeling for fitting the electrochemical impedance spectra data at different current densities.



**Fig. S3.** Electrochemical impedance spectra of nanofibre electrodes before and after the *ex situ* test. a) The esterified nanofibre electrode b) conventional nanofibre electrode (Test condition:  $\text{H}_2/\text{air}$  with gas flow rates of  $125/800 \text{ mL min}^{-1}$  at a current density of  $100 \text{ mA cm}^{-2}$ ).



**Fig. S4.** Electrochemical impedance spectra of the esterified nanofibre electrode (red circle) and the conventional nanofibre electrode (blue triangle). a) Nyquist plots, b) real capacitance plots, c) imaginary capacitance plots and d) the calculating  $R_{\text{ion}}$ . The test was performed at 0.4 V,  $\text{H}_2/\text{N}_2$  with gas flow rates of  $125/250 \text{ mL min}^{-1}$ , the cell temperature was  $65^\circ \text{C}$ , 100% RH, 1 bar.

The ionic resistance in the cathode is derived from a complex capacitance analysis.<sup>1, 2</sup> The complex capacitance can be expressed as<sup>3, 4</sup>

$$C(f) = \frac{1}{j2\pi f Z(f)} = \frac{1}{2\pi f [jZ'(f) - Z''(f)]} = -\frac{Z''(f)}{2\pi f |Z(f)|^2} - j\frac{Z'(f)}{2\pi f |Z(f)|^2} \quad \text{\* MERGEFORMAT (1)}$$

$$C'(f) = -\frac{Z''(f)}{2\pi f |Z(f)|^2} \quad \text{\* MERGEFORMAT (2)}$$

$$C''(f) = -\frac{Z'(f)}{2\pi f |Z(f)|^2} \quad \text{\* MERGEFORMAT (3)}$$

where  $C'(f)$  is the real capacitance and  $C''(f)$  is the imaginary capacitance. The double layer capacitance  $C_{\text{dl}}$  is calculated by numerical integration of  $C''(f)$  with respect to  $\log f$  as follows

$$\text{Area} = \int_{-\infty}^{\infty} C''(f) d \log f = 0.682 C_{\text{dl}} \quad \text{\* MERGEFORMAT (4)}$$

The ionic resistance  $R_{\text{ion}}$  can be calculated from the following equation

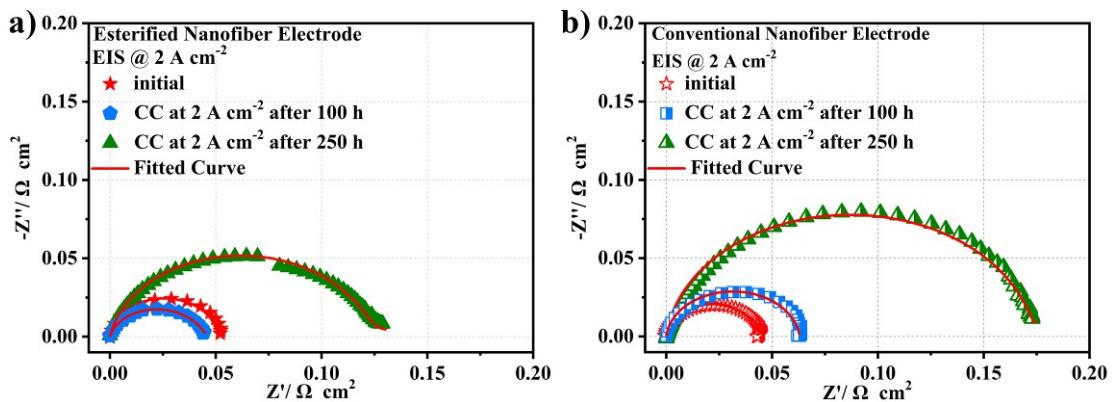
$$f_p = \frac{0.404}{\tau_{1,\text{max}}} = \frac{0.404}{R_{\text{ion}} C_{\text{dl}}} \quad \text{\* MERGEFORMAT (5)}$$

where peak frequency  $f_p$  corresponds to the peak in Fig. S4 c).

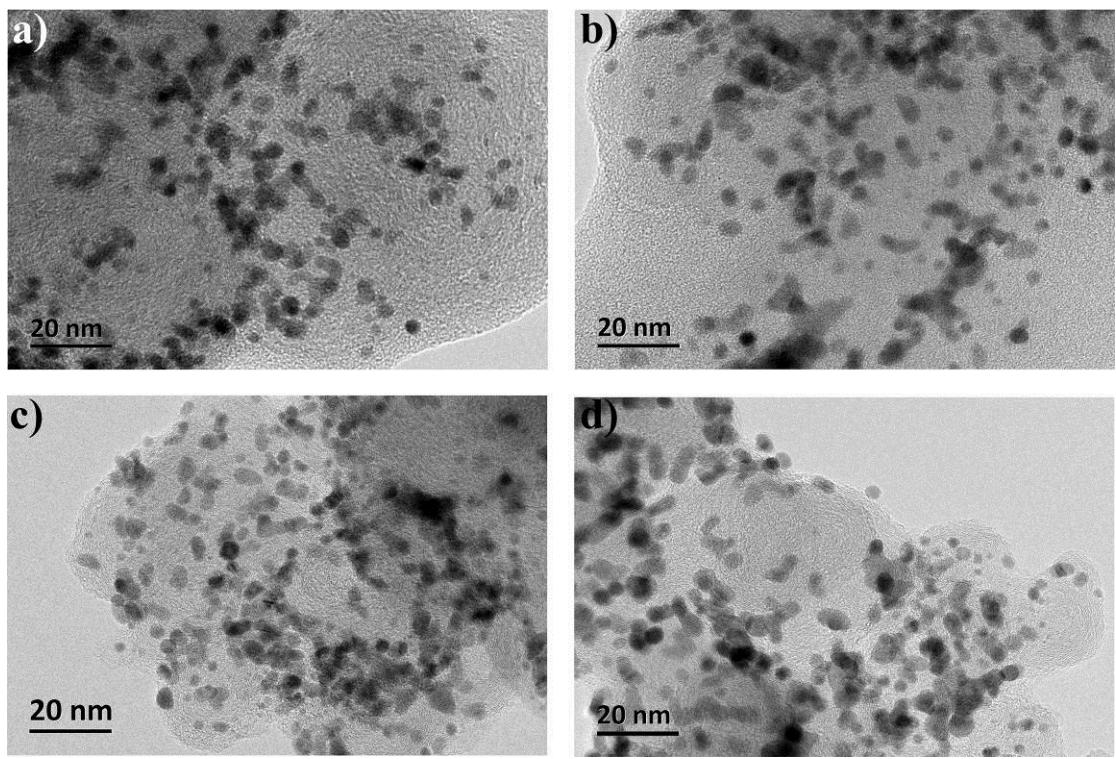
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**Table S1.** Electrochemical impedance parameters of the esterified nanofibre electrode and the conventional nanofibre electrode.

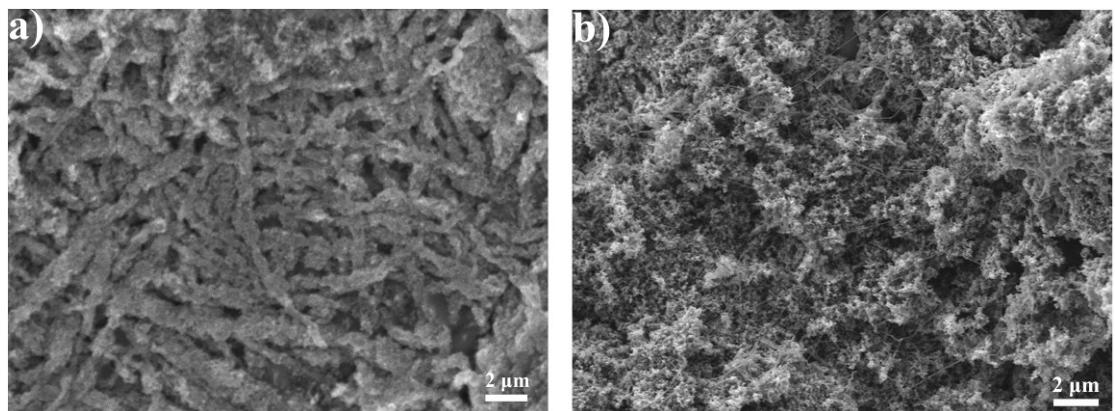
Samples	Integrated Area /mF cm <sup>-2</sup>	f <sub>p</sub> /Hz	C <sub>dl</sub> /mF cm <sup>-2</sup>	R <sub>ion</sub> /mΩ cm <sup>2</sup>
ENE	4.8	119	7.1	478
CNE	5.0	119	7.4	460



**Fig. S5.** Electrochemical impedance spectra of nanofibre electrodes before and after the *in situ* test. a) The esterified nanofibre electrode and b) the conventional nanofibre electrode in  $\text{H}_2/\text{O}_2$  condition with gas flow rates of  $125/250 \text{ mL min}^{-1}$  at a current density of  $2 \text{ A cm}^{-2}$ .



**Fig. S6.** TEM images of the esterified nanofibre electrode a) before and b) after the *in situ* operation. TEM images of conventional nanofibre electrode c) before and d) after the *in situ* operation.



**Fig. S7.** SEM images of the a) esterified nanofibre electrode and b) conventional nanofibre electrode after the *in situ* stability test.

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## References

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