

## Supporting Information

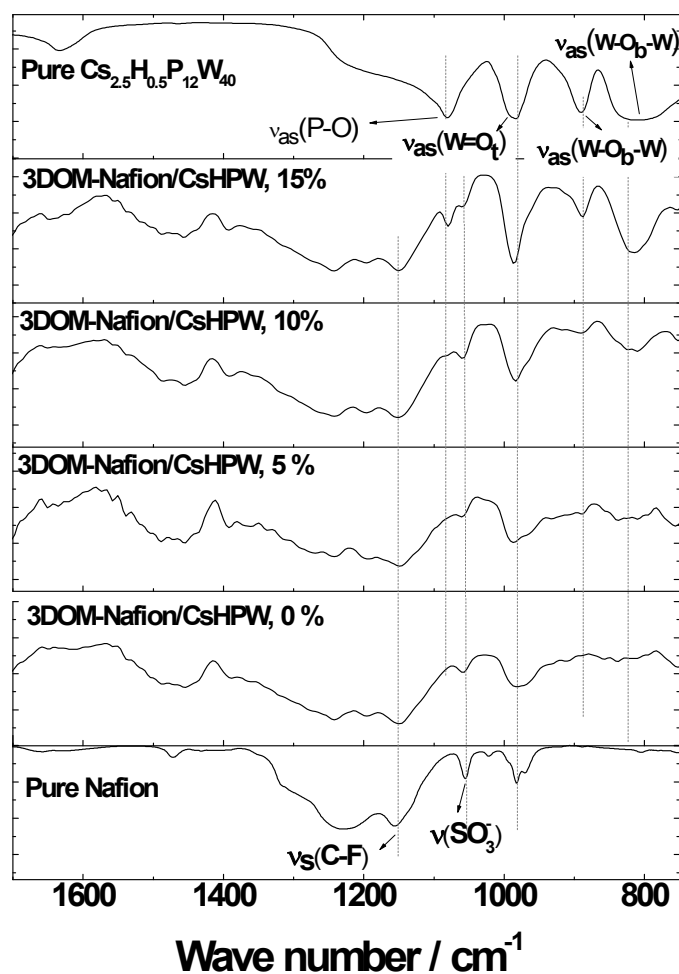
Highly ordered 3D macroporous scaffold supported Pt/C oxygen electrodes with superior proton-gas transportation properties and electrocatalytic activity for proton exchange membrane fuel cells

*Junsheng Li,<sup>a,b</sup> Haolin Tang,<sup>a\*</sup> Rui Chen,<sup>a</sup> Dan Liu,<sup>b</sup> Zhizhong Xie,<sup>b</sup> Mu Pan<sup>a</sup> and San Ping Jiang<sup>c</sup>*

<sup>a</sup>State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P. R. China.

<sup>b</sup>School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan, 430070, P. R. China.

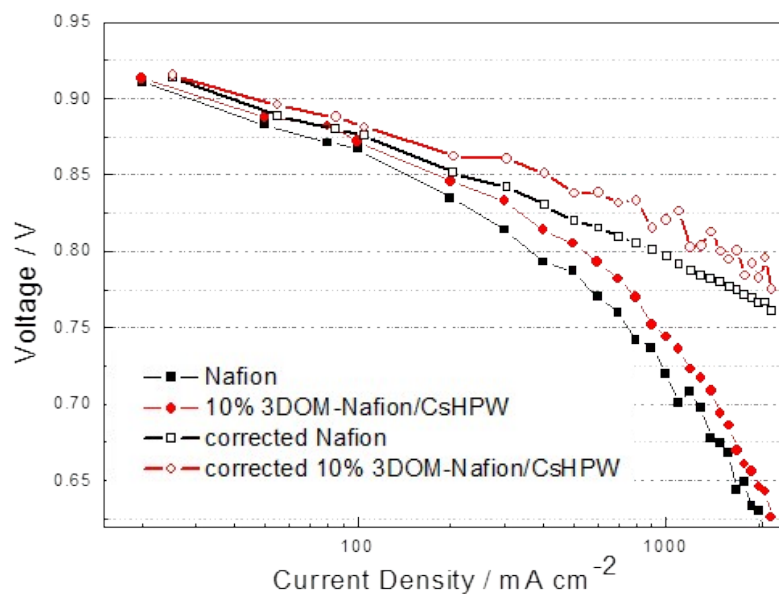
<sup>c</sup>Fuels and Energy Technology Institute & Department of Chemical Engineering, Curtin University, Perth, WA 6102, Australia.



**Figure S1.** Fourier transform infrared (FTIR) spectra of a recasted Nafion membrane, pure  $\text{Cs}_{2.5}\text{H}_{0.5}\text{P}_{12}\text{W}_{40}$  nanoparticle and 3DOM Nafion/CsHPW composites of different Nafion/ $\text{Cs}_{2.5}\text{H}_{0.5}\text{P}_{12}\text{W}_{40}$  contents.

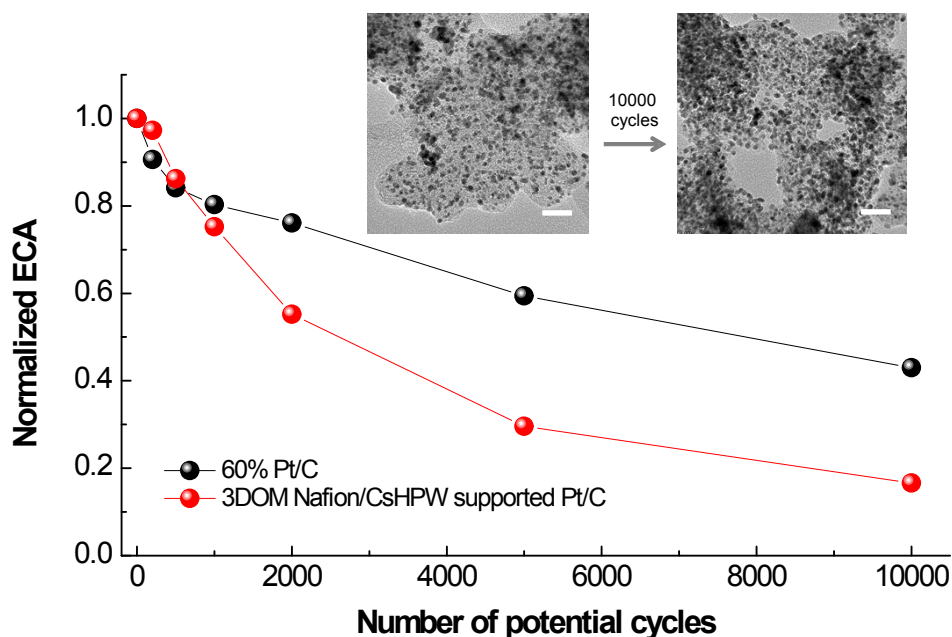
As depicted in Figure S1, characteristic absorption bands for the stretching vibration of the  $\text{W}=\text{O}_t$  ( $\text{O}_t$  refers to terminal oxygen) bond at  $\sim 985\text{ cm}^{-1}$ , the asymmetric stretching vibration of  $\text{W}-\text{O}_b-\text{W}$  bond ( $\text{O}_b$  refers to bridging oxygen) at  $894\text{ cm}^{-1}$  and the asymmetrical stretching vibration of the P-O group at  $1080\text{ cm}^{-1}$  are clearly visible in FTIR spectra of 3DOM Nafion/ $\text{Cs}_{2.5}\text{H}_{0.5}\text{P}_{12}\text{W}_{40}$  composites of different Nafion/ $\text{Cs}_{2.5}\text{H}_{0.5}\text{P}_{12}\text{W}_{40}$  concentrations. With the increase of the  $\text{Cs}_{2.5}\text{H}_{0.5}\text{P}_{12}\text{W}_{40}$  contents in the composite, the intensities of these characteristic peaks increased. The presence of these characteristic peaks demonstrated the Keggin structure of the phosphotungstate in the nanocomposite. Corresponding peaks from Nafion resin (asymmetric vibration of C-F bond at  $\sim 1150\text{ cm}^{-1}$  and symmetric stretching band at  $\sim 1060\text{ cm}^{-1}$ ) could be also identified from the FTIR spectra of the nanocomposites. A slight shift of the characteristic C-F bond toward low wave number was observed in the spectra of Nafion/ $\text{Cs}_{2.5}\text{H}_{0.5}\text{P}_{12}\text{W}_{40}$  composites, which may be resulted from the possible structural

rearrangement induced by the interaction between the nanoparticles and the side chains of Nafion within Nafion matrix.



**Figure S2.** Uncorrected and corrected performance of cells based on 60% Pt/C catalyst and 10% 3DOM-Nafion/CsHPW supported Pt/C catalyst.

Performance of the single cell based on 60% Pt/C catalyst and 10% DOM-Nafion/CsHPW supported Pt/C catalyst were evaluated at 80 °C using H<sub>2</sub> (s=2) and O<sub>2</sub> (s=9.5) as reactants. The pressure was controlled to be 1.5 bar on both anode and cathode during the test. Cell resistance was recorded by in situ EIS measurement at 1kHz. Hydrogen crossover current was also determined for the correction of the polarization curves (*Int. J. Hydrogen Energ.*, 2012, 37, 9782). The polarization curves of the cells before and after corrections are shown in Fig.S2. The current density of the cell at 0.9 V determined from the corrected polarization curve is 37.85 cm<sup>-2</sup> and 45.72 mA cm<sup>-2</sup> for Nafion and 3DOM-Nafion/CsHPW, respectively. The mass activity of the 3DOM-Nafion/CsHPW supported Pt/C catalyst was 0.183 A/g, higher than 0.154 A/g for the 60% Pt/C.



**Figure S3.** Changes in ECA of the catalyst as a function of cycling numbers during the durability test and TEM images (inset, scale bar 20 nm) of the 3DOM Nafion-CsHPW supported Pt/C catalyst before and after 10000 cycles.

The stability of the catalysts was measured using autolab electrochemical workstation (PG30/FRA, Netherlands) with a three-electrode configuration. A saturated calomel electrode (SCE) was used as the reference electrode, and platinum wire was used as the counter electrode. Voltammetric cycling between 0.3 and 0.9 V (vs. SCE) at a scan rate of 50 mV/s in 0.1 M HClO<sub>4</sub> were performed to the 3DOM Nafion-CsHPW supported Pt/C catalyst and 60% Pt/C catalyst. The results are shown in Fig.S3. The 3DOM Nafion-CsHPW supported Pt/C catalyst showed better stability in the beginning of the durability test, retaining 86.2% of the initial ECSA after 500 cycles from 0.3 V to 0.9 V (vs. SCE). This result indicates that the pore wall of the 3DOM Nafion prevents the aggregation of the Pt nanoparticles. However, the 3DOM Nafion-CsHPW supported Pt/C catalyst degraded more rapidly than the Pt/C catalyst after the first 500 cycles. The 3DOM Nafion-CsHPW supported Pt/C catalyst was fabricated without using Nafion solution as binder. In contrast, conventional Pt/C catalyst was bind with Nafion solution. Therefore, the Pt/C catalyst may have a higher integrality than the 3DOM Nafion-CsHPW supported Pt/C catalyst during long term operation. This may explain the lower stability of the 3DOM Nafion-CsHPW supported Pt/C catalyst observed from the CV cycling experiments.

**Table S1** Electrochemical activity surface area of the electrodes with conventional Nafion and 3DOM Nafion/Cs<sub>2.5</sub>H<sub>0.5</sub>P<sub>12</sub>W<sub>40</sub> nanocomposites.

Cs <sub>2.5</sub> H <sub>0.5</sub> P <sub>12</sub> W <sub>40</sub> Content / %	Q <sub>H</sub> / A*V	geometric area / cm <sup>2</sup>	Specific Active area / m <sup>2</sup> g <sup>-1</sup>
Nafion	0.0497	25	78.89
0% 3DOM-Nafion/CsHPW	0.0508	25	80.63
5% 3DOM-Nafion/CsHPW	0.0531	25	84.29
10% 3DOM-Nafion/CsHPW	0.0538	25	85.40
15% 3DOM-Nafion/CsHPW	0.0544	25	86.35

Table S2 lists the fitted impedance parameters for the O<sub>2</sub> reduction reaction on the asprepared cathode electrodes in the fuel cells. The coefficient,  $n$ , in the nonlinear least square fitting program for the constant phase element (CPE) was 0.91-0.94, very close to 1. This indicates that the simple resistance-capacitance equivalent circuit proposed for the reaction on the cathode electrode is valid. The exchange current density,  $j_o$ , can be calculated from the charge-transfer resistance in the linear region according to Equation S2.

$$R_{ct} = RT/nFj_o \quad (S2)$$

**Table S2** Fitted impedance parameters for the O<sub>2</sub> reduction on the electrodes with conventional Nafion and 3DOM Nafion/Cs<sub>2.5</sub>H<sub>0.5</sub>P<sub>12</sub>W<sub>40</sub> nanocomposites.

Cs <sub>2.5</sub> H <sub>0.5</sub> P <sub>12</sub> W <sub>40</sub> Content / %	DC bias / mAcm <sup>-2</sup>	geometric area / cm <sup>2</sup>	$n$	R <sub>e</sub> / Ω cm <sup>2</sup>	R <sub>ct</sub> / Ω cm <sup>2</sup>	$i$ /A cm <sup>-2</sup>
Nafion	200	25	0.93	0.022	0.103	0.3188
	600	25	0.91	0.021	0.061	0.5498
	1000	25	0.92	0.021	0.043	0.7689
0	200	25	0.95	0.014	0.058	0.5520
	600	25	0.93	0.013	0.048	0.6814
	1000	25	0.92	0.013	0.029	1.1401
5	200	25	0.94	0.013	0.06	0.5393
	600	25	0.91	0.012	0.046	0.7267
	1000	25	0.93	0.012	0.029	1.1278
10	200	25	0.94	0.011	0.059	0.5485
	600	25	0.93	0.01	0.044	0.7433
	1000	25	0.93	0.01	0.03	1.0902
15	200	25	0.94	0.011	0.053	0.6105
	600	25	0.92	0.01	0.033	1.0019
	1000	25	0.91	0.009	0.029	1.1526