

## Electronic Supplementary Information

### Vertically Oriented Polypyrrole Nanowire Arrays on Pd-plated Nafion<sup>®</sup>

#### Membrane and Its Application in Direct Methanol Fuel Cells

Zhangxun Xia, Suli Wang, Yongjiang Li, Luhua Jiang, Hai Sun, Shan Zhu, Dang Sheng Su and Gongquan Sun

#### Experimental Section

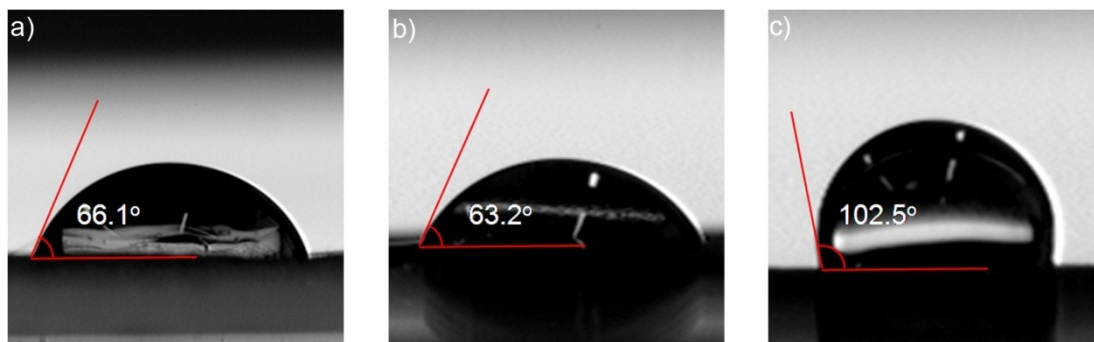
**Synthesis:** The preparation of Pd-plated Nafion<sup>®</sup> 115 membrane by electroless plating is described elsewhere.<sup>1</sup> The average loading of Pd deposited on the Nafion<sup>®</sup> membrane is about 1 mg cm<sup>-2</sup>. The PPy nanowire arrays were prepared by electrochemical polymerization. In brief, disodium hydrogen phosphate dodecahydrate (15.406 g, Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O, 99%, Tianjin Damao Reagent) and sodium phosphate monobasic dehydrate (6.240 g, NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O, 99%, Tianjin Damao Reagent) were dissolved in de-ionized water (200 mL) to prepare phosphate buffer solution (0.2 M, PBS); p-toluenesulfonyl (3.884 g, 98.5%, Tianjin Guangfu Reagent) was then dissolved in the as-prepared PBS; in which pyrrole (1.388 mL, 98%, Sinopharm Chemical Reagent) was dispersed by ultrasonication. The as-prepared Pd-plated Nafion<sup>®</sup> 115 membrane sealed by a plastic holder with Pt wire as electron conductor contacting with Pd membrane was used as the work electrode. A Pt plate (5×7 cm<sup>2</sup>) and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrochemical experiments were carried out by using an electrochemical workstation (SI1287, Solartron Co.). To electrochemically deposit PPy on Pd-membranes, the typical potential applied to the working electrode (Pd-membrane) was 0.65 V vs. SCE and kept for 30 min. After the polymerization, the working electrode was removed from the electrolyte and rinsed with de-ionized water, and then stored in de-ionized water for further characterization. The catalytic layer in anode was prepared by brushing a 60 wt. % PtRu/C (Johnson Matthey Co.) ink on the gas diffusion layer to obtain a metal loading of 3.6 mg cm<sup>-2</sup>. The catalyst coated membrane (CCM) in cathode was prepared by spraying Pt black (Johnson Matthey Co.) on PPy nanowire arrays coated Nafion<sup>®</sup> 115 membrane to obtain a metal loading of 0.5 mg cm<sup>-2</sup>. The MEAs with an active area of 2×2 cm<sup>2</sup> was fabricated by hot

pressing cathode CCM sandwiched between the anode GDE and the cathode gas diffusion layer at 120 °C and 200 kg cm<sup>-2</sup> for 1 min.

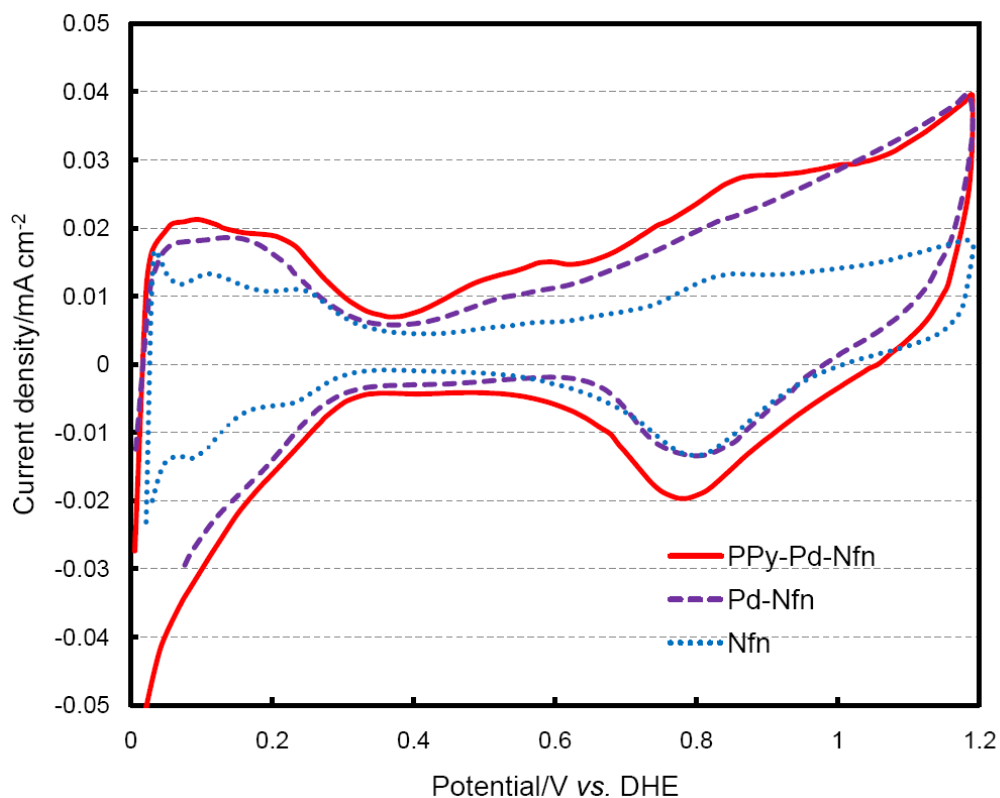
**Characterization:** Pd-plated Nafion<sup>®</sup> 115 membrane and PPy nanowire arrays were investigated by X-ray diffraction (XRD, D/max-2400X, Ricoh) spectra, field emission scanning electron microscope (FESEM, S-4800, Hitachi) and transmission electron microscope (TEM, JEM-2011EM, JEOL). The wetting behaviour and the sheet resistance of the samples were characterized by a contact-angle meter (JC2000C1, Shanghai Powereach) and a four point probe measurement (SZ-82, Suzhou Telecommunication), respectively. The single cell tests on DMFC were carried out by using a fuel cell test system (FCTS, Arbin Co.) and an electrochemical workstation (SI1287 and SI1260, Solartron Co.).

Reference:

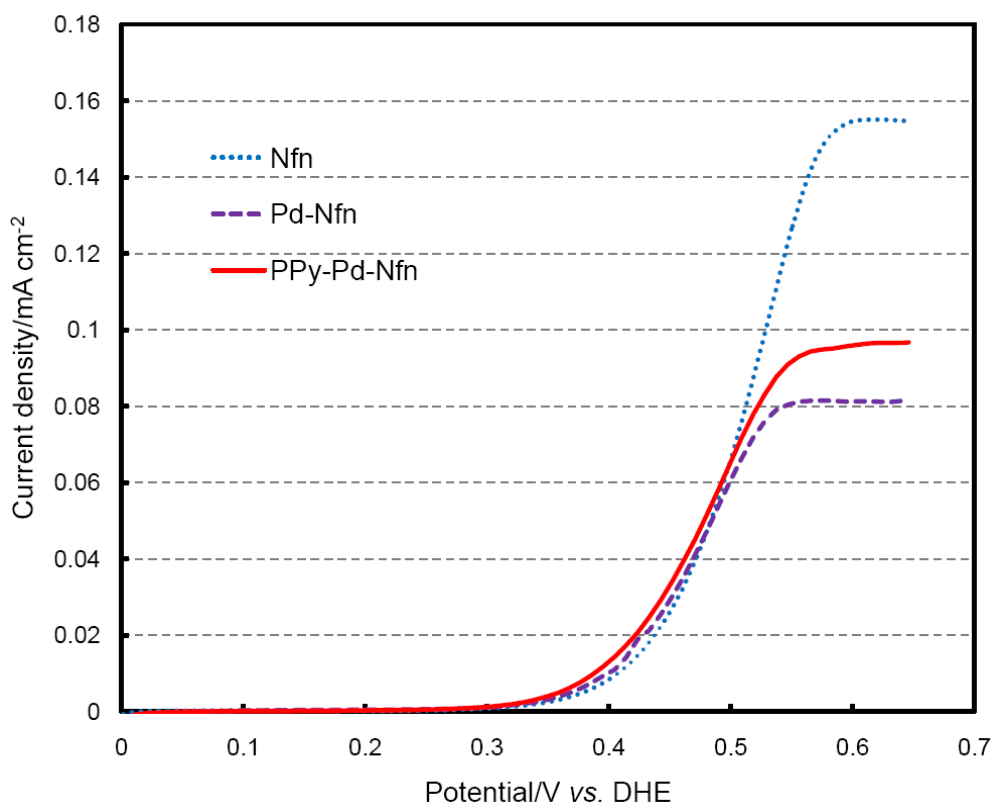
1 H. Sun, G. Sun, S. Wang, J. Liu, X. Zhao, G. Wang, H. Xu, S. Hou, Q. Xin, *J. Membr. Sci.*, 2005, **259**, 27.



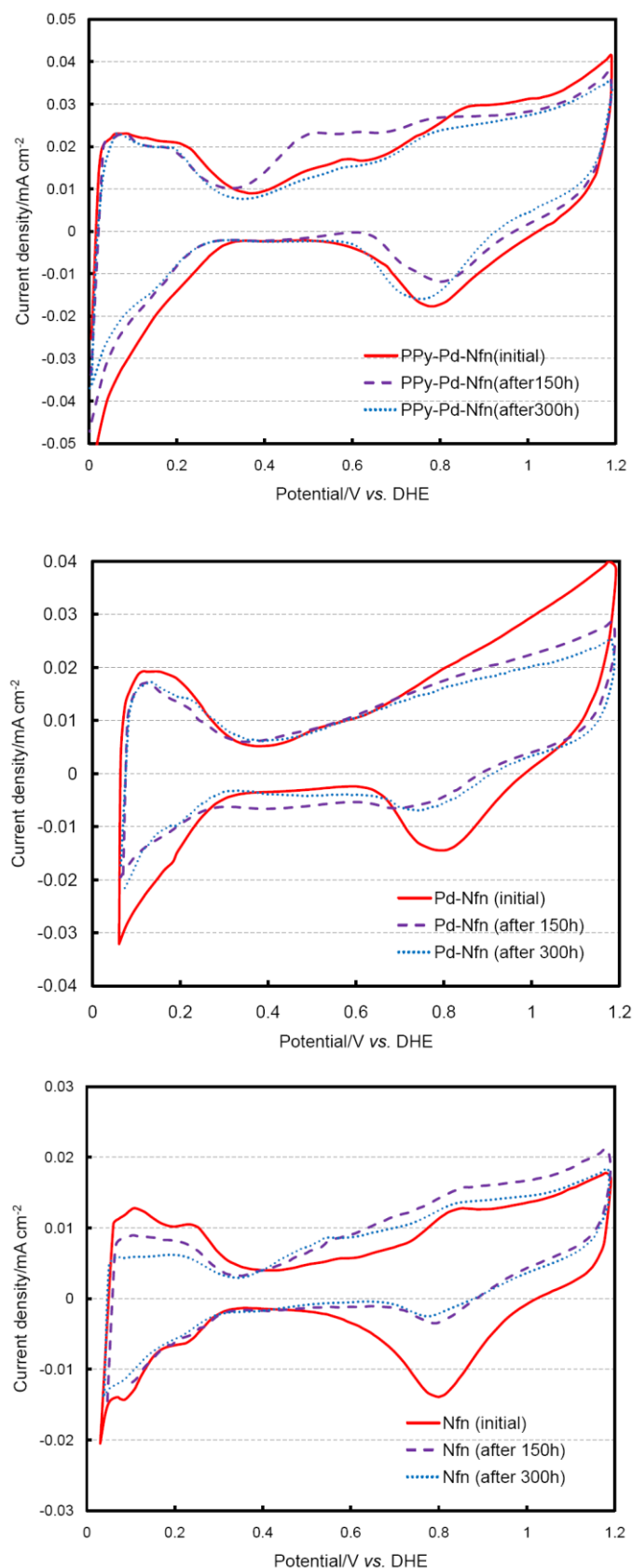
**Fig. S1** Photographs of wetting behaviors for different samples. a, Pd-activated Nafion<sup>®</sup> 115 membrane. b, Pd-plated Nafion<sup>®</sup> 115 membrane. c, PPy nanowire arrays on Pd-plated Nafion<sup>®</sup> 115 membrane.



**Fig. S2** Cyclic Voltammograms for cathodes of DMFCs. Cathodes with Nfn (short blue dashed), Pd-Nfn (long purple dashed) and PPy-Pd-Nfn (red solid line) are fed with de-ionized water at the flow rate of 1 mL min<sup>-1</sup>; anodes are fed with hydrogen at 50 mL min<sup>-1</sup>; the scan rate is 100 mV s<sup>-1</sup>; the cell temperature is 80 °C.



**Fig. S3** Methanol crossover currents for DMFCs with Nfn (short blue dashed), Pd-Nfn (long purple dashed) and PPy-Pd-Nfn (red solid line); cathodes are fed with N<sub>2</sub> at 80 mL min<sup>-1</sup>; anodes are fed with methanol solution (1 M aq.) at the flow rate of 1 mL min<sup>-1</sup>; the scan rate is 1 mV s<sup>-1</sup>; the cell temperature is 80 °C.



**Fig. S4** Cyclic Voltammograms before durability tests (red solid line), after 150 h durability tests (long purple dashed) and after 300 h durability tests (short blue dashed) for cathodes of DMFCs with a) Ppy-Pd-Nfn, b) Pd-Nfn and c) Nfn. Cathodes are fed with de-ionized water at the flow rate of 1 mL min<sup>-1</sup>; anodes are fed with hydrogen at 50 mL min<sup>-1</sup>; the scan rate is 100 mV s<sup>-1</sup>; the cell temperature is 80 °C.

**Tab. S1** ECSAs of Pt in the cathode of different MEA structures before and after 300 h durability tests.

Sample	Nfn		Pd-Nfn		PPy-Pd-Nfn	
	Initial	After 300 h	Initial	After 300 h	Initial	After 300 h
ECSA ( $\text{m}^2 \text{g}^{-1} \text{Pt}$ )	15.10	5.65	20.08	11.93	33.74	23.12

**Equation S1 and S2**

$$I_{cross} = I_{cross, ocv} (1 - I/I_{lim}) \quad (1)$$

$$\eta_{methanol} = I / (I + I_{cross}) \quad (2)$$

Where  $I$  is the current density of the cell;  $I_{cross}$  is the current density caused by methanol cross over at the current density of  $I$ ;  $I_{cross, ocv}$  is the limited current density of methanol cross over;  $I_{lim}$  is the limited current density of the anode;  $\eta_{methanol}$  is the methanol utilization at the current density of  $I$ .