

Electronic supplementary information (ESI)

CN_x nanofibers converted from polypyrrole nanowires as platinum support for methanol oxidation

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SI 1. Current densities (J) of Pt/CN_x, Pt/PPy and Pt/XC-72 catalysts representing the catalytic activity per active site

SI 2. Analysis on the degradation of Pt/PPy catalyst after immersion in electrolyte

SI 1. Current densities (J) of Pt/CN_x, Pt/PPy and Pt/XC-72 catalysts representing the catalytic activity per active site

The electrochemically active areas (EAA) of Pt/CN_x, Pt/PPy and Pt/XC-72 catalysts have been evaluated by hydrogen electrosorptions and CO stripping voltammetries, as shown in Fig. 8 in the main text.

EAA_H could be estimated by the formula:

$$EAA_H = Q_H / (0.21 \times L_{Pt}) \quad [\text{Ref. 13 in the main text}].$$

Here Q_H is the amount of charge change arisen from H-adsorption or H-desorption, constant 0.21 (mC/cm²) is the charge required to oxidize a monolayer of H₂ on a bright Pt, and L_{Pt} represents the platinum loading in the electrode. From the H-adsorption curves in Fig. 8a, Q_H of Pt/CN_x, Pt/PPy and Pt/XC-72 catalysts are obtained to be 8.3, 9.3 and 6.7 mC/cm². L_{Pt} is the same (38.5 μg /cm²) for the three catalysts. Hence, EAA_H(Pt/CN_x), EAA_H(Pt/PPy) and EAA_H(Pt/XC-72) are obtained to be 104, 117 and 84 (m²/g Pt), respectively.

Similarly, EAA_{CO} could be estimated from the formula of EAA_{CO} = $Q_{CO}/(0.484 \times L_{Pt})$ [Ref. 13a, 14 in the main text], and EAA_{CO}(Pt/CN_x), EAA_{CO}(Pt/PPy) and EAA_{CO}(Pt/XC-72) are obtained to be 92, 101 and 78 (m²/g Pt), respectively.

It is seen that both experimental results of hydrogen electrosorptions and CO stripping voltammetries show the relative order of EAA (Pt/PPy) > EAA (Pt/CN_x) > EAA (Pt/XC-72). This relative order suggest the average size d of Pt nanoparticles should have the relative order of d (Pt/PPy) < d (Pt/CN_x) < d (Pt/XC-72) since the Pt loading on the electrodes are the same (38.5 μg /cm²). This is indeed confirmed by HRTEM observation as shown in Fig. 6 (b,d,f) in the main text.

Based on the above results, the current densities (J) which represent the catalytic activity per active site have been estimated, and described below:

From the stable CV of the fresh catalyst (Fig. 9 in the main text), it is learnt that the maximum currents ($J_{\max} \times 0.071 \text{ cm}^2$) are 1.0, 0.49 and 0.32 mA for Pt/PPy, Pt/CN_x and Pt/XC-72 catalysts, respectively. Since the Pt loading for the three catalysts are all 2.73 μg (38.5 μg/cm²), when taking EAA_H as the electrochemically active area, the corresponding J' are obtained to be 3.13, 1.73 and 1.40 A/m². In detail:

$$J'(\text{Pt/PPy}) = 1.0 \text{ mA} \div (2.73\mu\text{g} \times 117 \text{ m}^2/\text{g}) = 3.13 \text{ A/ m}^2$$

$$J'(\text{Pt/CN}_x) = 0.49 \text{ mA} \div (2.73\mu\text{g} \times 104 \text{ m}^2/\text{g}) = 1.73 \text{ A/ m}^2$$

$$J'(\text{Pt/XC-72}) = 0.32 \text{ mA} \div (2.73\mu\text{g} \times 84 \text{ m}^2/\text{g}) = 1.40 \text{ A/ m}^2$$

When taking EAA_{CO} as the electrochemically active area, the corresponding current densities are obtained to be 3.62, 1.95 and 1.50 A/m². In detail:

$$J'(\text{Pt/PPy}) = 1.0 \text{ mA} \div (2.73\mu\text{g} \times 101 \text{ m}^2/\text{g}) = 3.62 \text{ A/ m}^2$$

$$J'(\text{Pt/CN}_x) = 0.49 \text{ mA} \div (2.73\mu\text{g} \times 92 \text{ m}^2/\text{g}) = 1.95 \text{ A/ m}^2$$

$$J'(\text{Pt/XC-72}) = 0.32 \text{ mA} \div (2.73\mu\text{g} \times 78 \text{ m}^2/\text{g}) = 1.50 \text{ A/ m}^2$$

It is seen that $J'(\text{Pt/PPy})$ is much larger than $J'(\text{Pt/CN}_x)$ catalyst, hence the much bigger peak current in the stable CV for the fresh Pt/PPy catalyst (see Fig. 9) not only comes from the larger EAA due to the smaller Pt size, but also from the modified chemical state of the Pt species by PPy probably due to the influence of abundant pyrrolic nitrogen. [Ref. 15 in the main text] Unfortunately, PPy nanowires are unstable in acid solution and easy for degradation as shown in our experiment, hence are not ideal support for DMFC. In contrast, Pt/CN_x catalyst is quite stable and its catalytic activity is better than that of Pt/XC-72 catalyst. Hence CN_x nanofibers are a new kind of carbon-based support with potential in DMFC.

SI 2. Analysis on the degradation of Pt/PPy catalyst after immersion in electrolyte

As known, CO poisoning is a usual reason for the activity degradation of electrocatalysts in DMFC. However, in this study, the deterioration of Pt/PPy results mainly from the degradation of PPy nanowires in acid solution rather than the CO poisoning, as learnt from the TEM observation (Fig. 7 in the main text) and CO stripping test. Fig. 7 shows obvious collapse for PPy nanowires while little change for CN_x nanofibers. The collapse of PPy nanowires could degrade their performance as electrocatalyst support due to, e.g., the decrease of electrical conductivity. From the CO stripping curves (Fig. 8b in the main text), it's seen that both the onset potential (E_{on} , 0.51 V) and anodic peak potential (E_{an} , 0.55 V) of Pt/PPy are slightly lower than the corresponding ones of Pt/CN_x (0.53 and 0.57 V). This means that the CO tolerance of Pt/PPy is comparable with or even better than that of Pt/CN_x. If the deterioration of Pt/PPy were caused by CO poisoning, it should also occur for Pt/CN_x in the same experimental condition. Hence the deterioration of Pt/PPy could be ascribed to the degradation of PPy nanowires in acid solution [Ref. 12 in the main text] rather than the CO poisoning.