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Vertically oriented polypyrrole nanowire arrays on Pd-plated Nafion® membrane and its application in direct methanol fuel cells†

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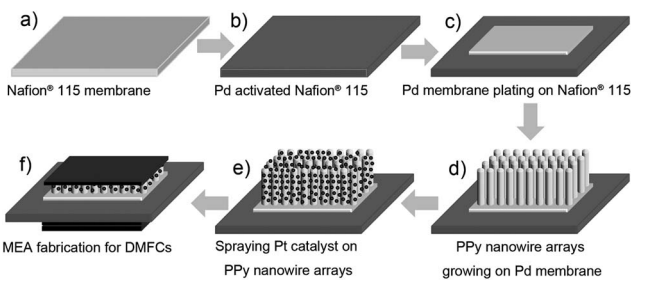
Highly ordered polypyrrole nanowire arrays are constructed *via* electrochemically polymerizing pyrrole directly on Pd-modified Nafion® membrane. A significant enhancement in the performance and durability of direct methanol fuel cells (DMFCs) is observed when such an ordered structure is used as an ordered electrode.

DMFCs, as a class of the most promising alternative energy conversion devices, have drawn special attention for their portability and fewer safety concerns because of the use of liquid fuels.[1] DMFCs have many advantages over hydrogen fuel cells, however, the relatively low performance, methanol crossover and massive use of precious metals are obstacles to the commercialization of DMFCs.[2] Great efforts have been made to solve these problems by synthesis of highly active catalysts, low methanol permeability membranes, and novel-structured membrane electrode assemblies (MEAs).[3] Among these efforts, the fabrication of MEAs with ordered structures in micro- and nano-scales is the frontier of fuel cell research.

The ordered-structured MEAs,[4] in which the electric conductor had catalysts and proton conductors coated on the outside oriented perpendicular to the membrane, were supposed to be able to maximize the utilization of catalyst and enhance the mass transfer of reactants/products and electrons/protons. Carbon nanotubes (CNTs),[5] tungsten oxide,[6] carbon coated tin[7] and organic crystalloid whiskers[8] were developed to form an ordered catalyst layer. However, the obvious drawback of the above substrates is the following hot-pressing process commonly used to transfer the catalyst layer could destroy the orderliness and orientation of the materials in MEAs. Furthermore, the processes for loading catalysts into the ordered structures, such as sputter deposition, suffer from the drawbacks of rigorous conditions, high cost and so on.

To build up a MEA with an ordered-structure, the most straightforward way is to fabricate such a structure directly on proton exchange membranes. However, due to the electronic insulation of Nafion® membrane, it still remains in challenge to modify the polymer membrane using the widely used electrochemical methods for further fabrication of ordered structures. In this communication, for the first time, we report a facile method to fabricate vertically oriented nanostructures by electrochemically growing polypyrrole (PPy) nanowire arrays with highly electronic conductivity directly on a Pd-modified proton exchange membrane. The fuel cell fabricated with these materials shows a significantly improved performance and durability compared to that with a conventional MEA.

As illustrated in Scheme 1, a piece of Nafion® 115 membrane was electroless plated with Pd,[9,10] and then PPy nanowire arrays were electrochemically polymerized on the Pd substrate. After spraying



Scheme 1 Fabrication process for PPy nanowire arrays and MEAs for DMFCs. (a) Nafion® 115 membrane pre-treated by H_2O_2 and H_2SO_4. (b) The pre-treated Nafion® 115 membrane is activated by a divalent palladium complex and reducer. (c) The Pd membrane is chemically plated on the activated Nafion® 115 membrane. (d) PPy nanowire arrays are grown on pre-prepared Pd membrane by electrochemical polymerization. (e) Pt black catalyst ink is sprayed on PPy nanowire arrays to form the cathode catalyst layer. (f) MEAs are fabricated by sandwiching the as-prepared cathode catalyst layer between the diffusion layer and the anode.

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the Pt black catalyst ink on the ordered PPy, the MEA was fabricated for the single cell tests. The same amount of Pt black was sprayed on the pristine Nafion® 115 membrane and Pd-plated Nafion® membrane, respectively, which were then used to fabricate single cells for comparison. The Nafion® 115 membrane, Pd-plated Nafion® membrane and membrane coated with PPy nanowire arrays are denoted as Nfn, Pd-Nfn and PPy-Pd-Nfn, respectively. The experimental details are described in the ESI.†

The morphology of the Pd membrane surface is shown in Fig. 1a. Pd nano-islands with a mean size of 20–30 nm are formed by the congregation of the primary Pd particles. Such Pd nano-islands could act as the nucleation sites for the electrochemical polymerization of pyrrole. Fig. 1b–f are SEM and TEM images of the PPy-Pd-Nfn sample. During the synthesis, pyrrole monomers are first electro-oxidized to oligomers at the surface of the Pd-plated Nafion® membrane, which was used as the working electrode. Then, with the help of a soft-template, such as $H_2PO_4^-$, HPO_4^{2-} and TsO^-, conglomerations of PPy chains are formed through hydrogen bonding and electrostatic attraction between pyrrole oligomers and electrolyte ions. Finally, the conglomerations are inclined to vertical polymerization at the nucleation sites to vertically distribute the electric field.[11]

The different magnification images (Fig. 1b and c) show clearly that the extremely uniform arrays are constructed by the vertically aligned PPy nanowires directly on the Pd substrate. The closer upper-side view images of PPy nanowire arrays (Fig. 1d and e) at the cracked part of the membrane surface and the TEM image of the separated PPy nanowires (Fig. 1f) reveal more details of the morphology. The average length and diameter of the nanowire are around 600 and 110 nm, respectively. The average distance between the two adjacent nanowires is around 40 nm, and hence the growth density of the nanowire arrays is about 5×10^9 cm^{-2}. The X-ray diffraction patterns of Pd-plated Nafion® 115 membrane and PPy nanowire arrays as shown in Fig. 2, with peaks situated at approximately 16.9, 22.3 and 40.1°, are typical characteristics of Nafion®, PPy and Pd, respectively, as reported elsewhere.[12] The main peak for PPy at 22.3° giving *d*-spacing of 0.398 nm is attributed to the interplanar van der Waals distance of PPy chains, which is very close to the value previously reported for the electrochemically synthesized PPy.[13] However, unlike the broad asymmetric diffraction peak of the amorphous PPy reported in ref. 13, the peak for PPy nanowires is relatively sharp, suggesting a well-crystallized structure caused by an ordered polymerization process.

To investigate the suitability and feasibility of the PPy nanowire arrays applied in fuel cell electrodes, the wetting behaviour and electronic conductivity of the PPy nanowire arrays were tested by measuring the contact angles and sheet resistance, respectively. Pd-activated and Pd-plated Nafion® membrane have a similar wetting behaviour, being hydrophilic with contact angles less than 90°. In contrast, PPy nanowire arrays are much more hydrophobic with a contact angle of 102.5° (Fig. S1†), indicating that PPy nanowire arrays are suitable as supports for the cathode catalyst layer, benefitting from the advantage of its hydrophobicity, thus facilitating the mass transfer of the oxygen and water in the cathode.[14] PPy nanowire arrays also exhibit sufficient electronic conductivity of 53 S cm^{-1}, as shown in Table 1, which is in the same order as that of the doped PPy.[15]

The fabrication of the MEAs with the three membrane samples (Nfn, Pd-Nfn and PPy-Pd-Nfn) is described in the Experimental section. Cyclic voltammograms (CV), as shown in Fig. S2,† are employed to obtain electrochemical surface areas (ECSA) of the cathode Pt black catalyst according to the hydrogen adsorption

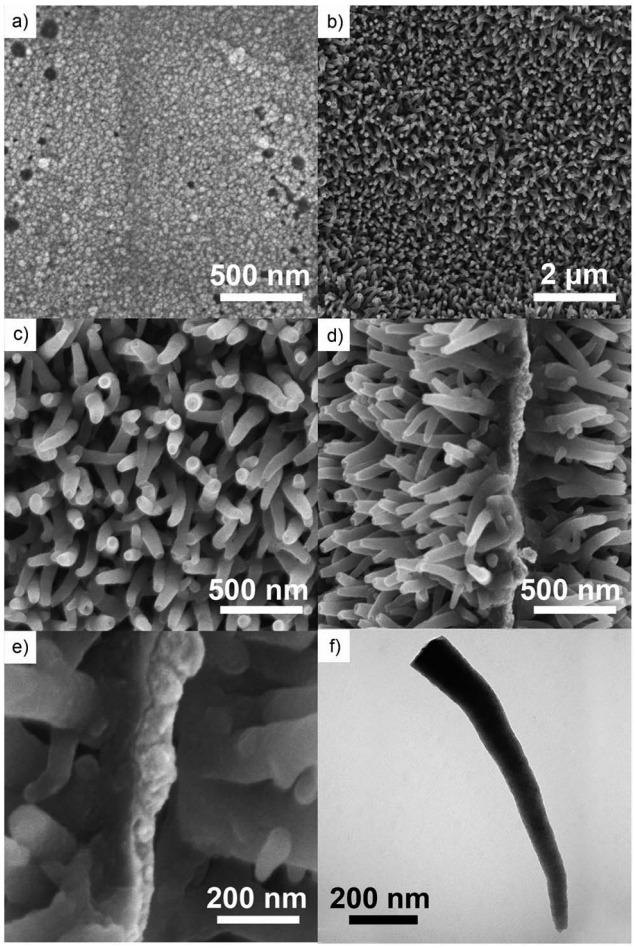

Fig. 1 SEM (a–e) and TEM (f) images of Pd membrane and PPy nanowire arrays. (a) Top view of Pd membrane plated on Nafion® 115. (b and c) Top views of well oriented PPy nanowire arrays on the Pd-plated membrane with different magnifications. (d and e) Side views of PPy nanowire arrays at the cracked part of the membrane. (f) TEM image of PPy nanowires.

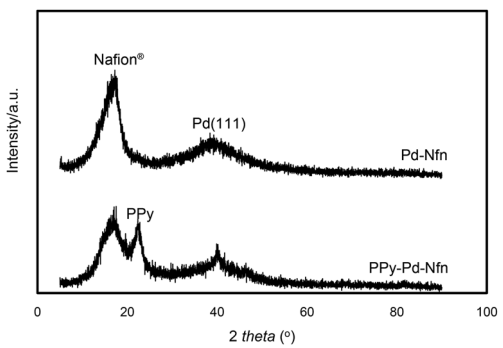

Fig. 2 XRD patterns of Pd-Nfn and PPy-Pd-Nfn.

Table 1 Electronic conductivity of different membranes[a]

Sample	Pd-activated Nafion® 115	Pd-Nfn	PPy-Pd-Nfn
Electronic conductivity S^{-1} cm^{-1}	0.298	869.565	53.050

[a] Three different points were tested for every sample, and the mean value is taken.

charges by using the conversion factor of 210 μC cm^{-2}.[16] The results are listed in Table 2. The ECSA of the Pt black catalyst sprayed on PPy nanowire arrays increased by 120% compared with that of the traditional CCM cathode structure. The ECSA of Pt on PPy can surprisingly reach 95% of the BET surface area of the Pt black catalyst by eliminating the effect of Pd membrane,[17] suggesting a high utilization of Pt in the electrode, in contrast, the utilization of Pt catalyst in the Nafion® membrane sample is only 50%. This great improvement in Pt utilization might be attributed to the improvement of the Pt particle distribution in the catalyst layer for the nanowire array structure. Additionally, around 40% reduction in the limiting current of methanol crossover is observed after introducing Pd to the Nafion® membrane, as shown in Fig. S3.† This improvement raises the methanol fuel utilization from 45% (Nfn) to 61% (Pd-Nfn) and 58% (PPy-Pd-Nfn) at the current density of 100 mA cm^{-2} (see eqn S1 and S2†).

Fig. 3 compares the single cell performance of DMFCs with the three MEAs. Polarization and power density curves show an increase in DMFC performance in the sequence of Nfn, Pd-Nfn and PPy-Pd-Nfn (Fig. 3a). The maximum power density of the single cell with PPy-Pd-Nfn is 104 mW cm^{-2}, which is enhanced by 45% compared to that of DMFC with Nfn. The improvement in the single cell performance with Pd-Nfn, compared to that with Nfn, can be primarily attributed to the suppression of methanol crossover through the Pd membrane. A more significant enhancement in cell performance, observed for the DMFC with PPy-Pd-Nfn compared to that with Pd-Nfn, is caused by introducing the ordered PPy nanowire arrays to the cathode electrode. Further investigation of the cathode polarization curves (Fig. 3b) reveals that the DMFC with PPy-Pd-Nfn shows superior performance compared with others in both the electrochemical polarization region and the mass transfer polarization region. The improvement in the electrochemical region can be attributed to the great enhancement in the ECSA of Pt, benefiting from the unique ordered structure as shown in Fig. S2† and listed in Table 2. The improvement in performance at the mass transfer region can be attributed to the facilitation of oxygen and water transfer due to the vertical pathways constructed by the ordered PPy nanowire arrays and the hydrophobic property of the PPy arrays.

Uncharacteristically for a traditional DMFC with Nfn, the DMFC with PPy-Pd-Nfn displays a striking durability, showing no

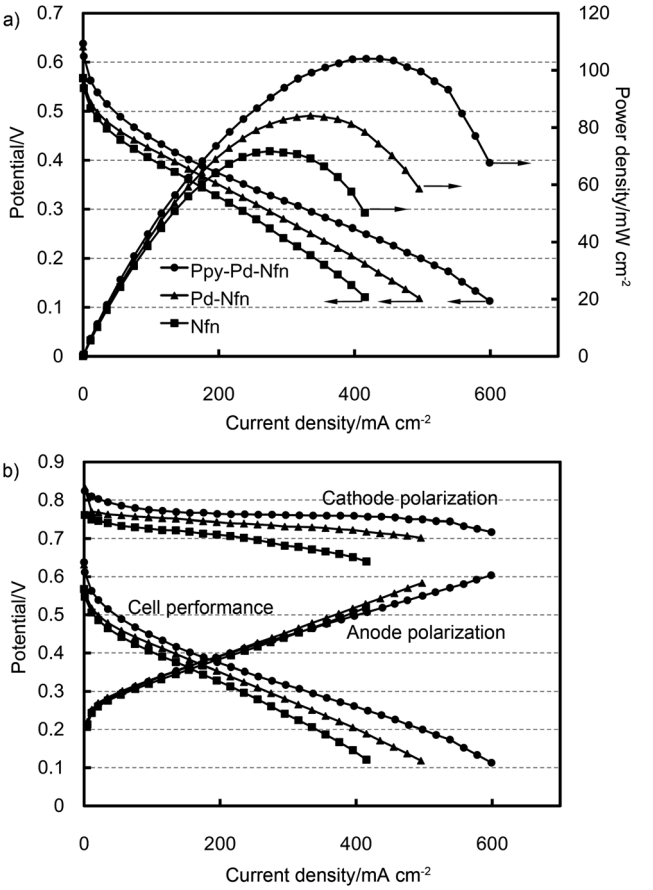

Fig. 3 DMFC polarization curves. (a) Polarization and power density curves for DMFCs with Nafion® 115 membrane (triangles), Pd-plated Nafion® 115 membrane (squares) and PPy nanowire arrays membrane (circles). (b) Anodic, single cell and calculated cathodic polarization curves for the three DMFCs. The cell temperature is 80 °C; flow rates of methanol solution (1.5 M aq.) and oxygen (0.1 MPa backpressure) is 1 mL min^{-1} and 100 mL min^{-1}, respectively.

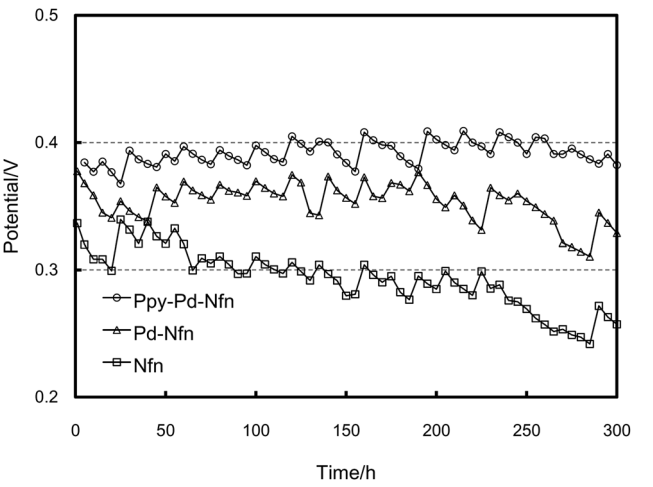

Fig. 4 Long-term performance curves at a constant discharging current of 100 mA cm^{-2} for DMFCs with Nafion® 115 membrane (squares), Pd-plated Nafion® 115 membrane (triangles) and PPy nanowire arrays membrane (circles). The cell temperature is 80 °C; flow rates of methanol solution (1.5 M aq.) and oxygen (without backpressure) at 1 mL min^{-1} and 40 mL min^{-1}, respectively.

Table 2 ECSA of Pt in the cathode of different MEA structures

Sample	Nfn	Pd-Nfn	PPy-Pd-Nfn
ECSA (m^2 g_{Pt}^{-1})	15.10	20.08	33.74

performance drop after a 300 h life-time test (Fig. 4). Additionally, the ECSA of Pt for the cathode catalyst layer with the sample PPy-Pd-Nfn lost only 31.5%, which is apparently less than those observed for the DMFCs with Pd-Nfn and Nfn (42.6% and 62.6%), respectively (Fig. S4 and Table S1†).

Conclusions

In summary, we have developed a simple method to fabricate PPy nanowire arrays with a highly ordered structure directly on the Pd-decorated proton exchange membrane, for fuel cells. This novel ordered MEA shows an excellent cell performance with a 45% enhancement in the maximum power density and a high stability, compared with the MEA with the traditional disordered structure. We believe that the significantly improved cell performance is due to (i) the enhancement of the Pt utilization and mass transfer of reactant/products, and (ii) alleviation of methanol crossover through the Pd membrane and the PPy nanowire arrays. This research is a pioneering work in the ordered MEA structures reported a decade ago. Our work provides a brand new idea to construct ordered MEAs for fuel cells directly on polymer electrolyte membranes. Additionally, the basic structure and experimental data reported in this work are also provided for further theoretical and modeling studies of the ordered MEAs. Besides its contribution to the development of proton exchange membrane based fuel cells, this research will also appeal the interest of scientists developing ordered nanostructures and understanding the mechanism of formation of such an ordered structure.

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