



Controllable synthesis of vertically aligned polypyrrole nanowires as advanced electrode support for fuel cells



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HIGHLIGHTS

- The morphology of the PPy nanowires grown on Pd modified Nafion[®] membranes can be controlled.
- The hydrophobicity/hydrophilicity of the PPy nanowires is related with the morphology.
- The enhancement of catalyst utilization is observed with the application of the PPy nanowires as cathode support in DMFCs.
- The most ordered PPy as the support of cathode for DMFCs displays the best performance due to the facile mass transport.

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ABSTRACT

Here, we develop a facile electrochemical polymerization method for the synthesis of polypyrrole (PPy) nanowires on Pd modified Nafion[®] membranes. Interestingly, with altering the deposition potential and temperature, we can easily tune the PPy nanowires from disordered nanostructures to well ordered vertically aligned nanowires. The various PPy nanowires show similar electronic conductivity but diverse hydrophobicity/hydrophilicity. The ordered PPy nanowires can significantly facilitate the mass transport and enhance the catalyst utilization. These two factors together make an obvious performance improvement of fuel cells.

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1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC), which converts chemical energy directly to electricity, is one of the most promising clean energy technologies attracting great research interests from 1990s. [1–4] Membrane electrode assembly (MEA), as the key component of fuel cells, acts as a complicated system which involves transports of both liquid and gaseous reactants/products. Thus performance of fuel cells significantly depends on the microstructure of the electrode, i.e., tailoring the micro- and macro-structure of the cathodic electrode can largely improve the oxygen and water transports. [5–7] Traditional electrodes with disordered microstructures lead to both poor mass transport of reactants/products and low utilization of catalyst, which has

already become a major bottleneck for further enhancement of fuel cell performances.

Ordered-structured MEA, proposed by Middelmann as early as 2002, [8] in which the electronic conductor loaded with catalysts and proton conductors coated outside orientates perpendicularly to the membrane, is supposed to be able to maximize the utilization of catalyst and greatly enhance the mass transport of reactants/products and electrons/protons. Recently, MEAs with ordered nanostructures have been developed based on various materials, such as carbon nanotube arrays, organic crystalloid whiskers and conductive polymer nanowire arrays. [9–15] However, to our knowledge, the fabrication of such ordered-structured materials as MEAs is still far from facility. Our previous paper reports a facile fabrication of vertically oriented polypyrrole (PPy) nanowire arrays on modified Nafion[®] membranes via electrochemical polymerization, which is confirmed a promising electrode material for direct methanol fuel cells (DMFCs). [16] However, the growth mechanism and the morphological controllability of the ordered PPy are still undiscovered.

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In this work, facile approaches to control the morphology of the PPy nanowires are put forward and the growth mechanism of the PPy nanowires on Pd-modified Nafion[®] membranes is proposed. The properties, such as wetting behaviors and electronic conductivities, of the PPy nanowires with various morphologies are investigated. The PPy nanowires on Nafion[®] membranes as cathode supports are fabricated, and the dependence of DMFC performances on the morphologies of the PPy nanostructures is discussed.

2. Experimental

2.1. Preparation of the PPy nanowires on Pd/Nafion[®] membranes

The experimental details of modification of Nafion[®] membrane with Pd could be found in our previous work. [17] In brief, a piece of Nafion[®] 115 membrane (DuPont) was immersed in Pd activation solution, and then rinsed with de-ionized water. The membrane was then immersed in borane dimethylamine complex (97%, Alfa Aesar) solution (1 mg mL⁻¹, aq.) for 5 min. The as prepared Pd activated Nafion[®] 115 membrane was then immersed in Pd chemical plating solution (Palatec) at 52 °C for 20 min. The as-prepared Pd-modified Nafion[®] membrane was denoted as Pd/Nafion[®].

The PPy nanowires were prepared via electrochemical polymerization controlled by an electrochemical workstation (SI1287, Solartron Co.). The Pd/Nafion[®] membrane sealed by a plastic holder with Pt wire as electron conductor contacting with Pd membrane was used as the working electrode. A Pt plate (5 × 7 cm²) and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrolyte solution for electrochemical polymerization was prepared as follows: 15.406 g disodium hydrogen phosphate dodecahydrate (Na₂HPO₄·12H₂O, 99%, Tianjin Damao Reagent) and 6.240 g monosodium phosphate dihydrate (NaH₂PO₄·2H₂O, 99%, Tianjin Damao Reagent) were dissolved in 200 mL de-ionized water to prepare 0.2 M phosphate buffer solution (PBS); 3.884 g *p*-toluenesulfonyl sodium (98.5%, Tianjin Guangfu Reagent) was then dissolved in 200 mL PBS; 1.388 mL pyrrole (98%, Sinopharm Chemical Reagent) was dispersed in the above solution by ultrasonication. The electrochemical polymerization of pyrrole was realized by applying a constant potential, e.g., 0.60, 0.65, 0.70, 0.75, 0.80 and 0.85 V vs. SCE on the working electrodes for 1800s at 278 K. The obtained PPy nanowires on Pd/Nafion[®] samples were denoted as PPy-E60, PPy-E65, PPy-E70, PPy-E75, PPy-E80 and PPy-E85, respectively. To study the effect of the electrolyte temperature on the morphology, the temperature was kept at 278, 298 and 318 K while the potential applied on the working electrode was controlled at 0.65 V vs. SCE. Accordingly, the obtained samples were denoted as PPy-T278, PPy-T298 and PPy-T318, respectively.

2.2. Fabrication of MEAs

To investigate the effect of the PPy nanowire morphologies on performance of DMFCs, the MEAs with different PPy samples applied as cathodes were fabricated as follows. By spraying catalyst ink composed of commercial Pt black (Johnson Matthey Co.) on the PPy nanowires, the cathode with a Pt loading of 0.5 mg cm⁻² was obtained. By brushing catalyst ink composed of a commercial 60 wt.% PtRu/C (Johnson Matthey Co.) on the gas diffusion layer (GDL), the anode with a PtRu loading of 3.6 mg cm⁻² was obtained. The MEAs with an active area of 2 × 2 cm² was fabricated by hot pressing the catalyst coated membrane of cathode sandwiched between the anode and the cathode gas diffusion layer at 120 °C and 200 kg cm⁻² for 1 min. The MEAs with PPy nanostructures of PPy-E65, PPy-E75 and PPy-E85 applied to the cathode were

denoted as MEA-E65, MEA-E75 and MEA-E85, respectively. For comparison, the traditional MEA with pristine Nafion[®] 115 membrane was denoted as MEA-T.

2.3. Characterization of the PPy nanowires on Pd/Nafion[®]

The morphologies of the PPy nanowire samples were investigated by field emission scanning electron microscope (FESEM, S-4800, Hitachi) and transmission electron microscope (TEM, JEM-2011EM, JEOL). The wetting behaviors of the PPy layers were measured by a contact-angle meter (JC2000C1, Shanghai Powereach), and the sheet resistances of the surfaces were characterized by a four point probe measurement (SZ-82, Suzhou Telecommunication).

2.4. DMFC Single cell performance tests

The CV curves of cathode were recorded by an electrochemical workstation (SI1287 and SI1260, Solartron Co.) at 80 °C. The cathode fed with de-ionized water at a flow rate of 1 mL min⁻¹ is used as the working electrode and the anode fed with hydrogen at a flow rate of 50 mL min⁻¹ used as both reference and counter electrode. The scan rate is 20 mV s⁻¹. The anode polarization curves were recorded by the electrochemical workstation (SI1287 and SI1260, Solartron Co.) at 80 °C. The anode fed with 0.5 M methanol solution at a flow rate of 1 mL min⁻¹ is used as the working electrode and the cathode fed with hydrogen at a flow rate of 50 mL min⁻¹ is used as both reference and counter electrode. The scan rate is 2 mV s⁻¹. The discharging curves (*I*–*V*) of DMFCs were evaluated by a fuel cell test system (FCTS, Arbin Co.) under an oxygen back pressure of 0.2 MPa and methanol concentration of 0.5 M. The working temperature of the single cells is 80 °C. The flow rates of oxygen and methanol solution is 80 mL min⁻¹ and 1 mL min⁻¹, respectively. The oxygen gain of DMFCs was the difference of the cell voltages at the same current density when the cathode was fed with oxygen or air (without back pressures).

3. Results and discussion

3.1. Controllable growth of the PPy nanowires

To understand the growth processes of the PPy nanowires over Pd/Nafion[®] membranes, a typical chronoamperometric curve

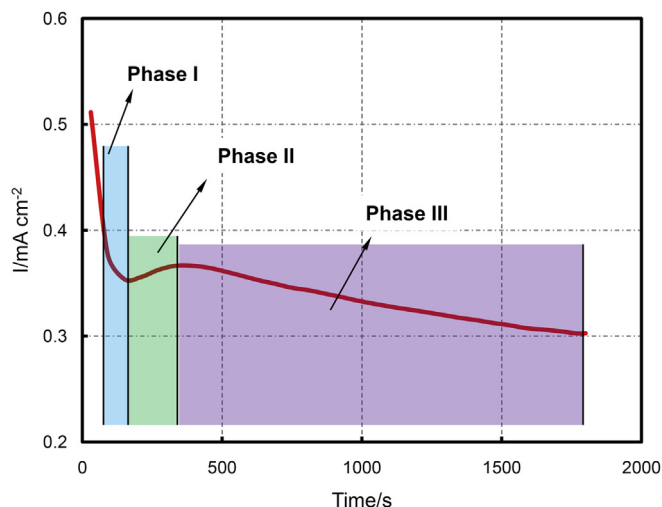


Fig. 1. A typical chronoamperometric curve of the synthesis of the PPy nanowires.

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