



High performance platinum nanorod assemblies based double-layered cathode for passive direct methanol fuel cells



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HIGHLIGHTS

- A double-layered cathode based on Pt nanorod assemblies was fabricated.
- Pt nanorods formed a network on top of the commercial Pt/C layer.
- An ESA increase of ~50% was observed for the double-layered cathode.
- Significant reduction of Pt loading up to 50% was achieved for the DMFCs.

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ABSTRACT

Reduction of the precious metal catalyst loading, especially in the cathode, is critical for the development of passive direct methanol fuel cells (DMFCs). Herein, a Pt nanorod assemblies based double-layered cathode is reported with significant catalyst loading reduction up to 50%. The nanorods, consisting of linear aggregates of Pt nanoparticles, are prepared from platinum carbonyl complexes and assembled on top of a Pt/C catalyst layer for the double-layered cathode fabrication. The maximum power density of a passive DMFC with the double-layered cathode, using 2.0 M methanol and at a temperature of 25 °C, is ca. 39.4 mW cm⁻² at a Pt loading of 2.0 mg cm⁻²; and it is ca. 29.1 mW cm⁻² at a Pt loading of 1.0 mg cm⁻² comparable to that with only a conventional Pt/C layer at a Pt loading of 2.0 mg cm⁻². The improved cell performance is ascribed to increased catalyst utilization and decreased charge-transfer resistance in the double-layered cathode as confirmed by electrochemical characterization and equivalent circuit analysis. The Pt nanorod assemblies based systems hold great potential for the cost reduction of DMFCs.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising micro- and portable electronic power sources owing to their high power density, low pollution and easy fuel refilling [1–5]. However, the commercialization process of DMFCs is impeded by the high content of the noble metals in membrane electrode assemblies (MEAs), which is in particular due to the high loadings of Pt-based catalysts [5–7]. Thus, the reduction of catalyst loading has been a key research focus for the development of DMFCs.

To reduce the catalyst loading on the anode, several approaches have been reported including the preparation of novel diffusive layer [8,9], formation of porous structure in the anode using removable nanoparticles [10], electrospinning [11], and other means [12]. It is believed that above approaches can facilitate the mass transfer in the anode and maximize the catalyst utilization, effectively reducing the anodic catalyst loading from 4.0 mg_(Pt-Ru) cm⁻² to 1.0 mg_(Pt-Ru) cm⁻² for passive DMFCs, while maintaining nearly the same cell performance. However, the cathode catalyst loading is still high, which is typically around 4–7 mg_(Pt) cm⁻², and approaches on how to reduce the Pt loading on the cathode for DMFCs remain limited. So far, many groups have focused on the preparation Pt nanocrystals and structures with special morphology, and it has been demonstrated the morphology

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of the nanocrystals are key factors in determining the catalytic activity and stability, such as Pt nanoparticles of different shapes [13–16], nanorods [17–19], and nanowires [20–22]. But the application of such catalysts in DMFCs has not been reported, neither their effects on catalyst loading reduction.

Herein, Pt nanorod assemblies are fabricated and utilized in the cathode of DMFCs in a double-layered configuration. The composition, crystallinity and morphology of the Pt nanorods were investigated in detail. Furthermore, a double-layered cathode (DLC) for the DMFCs fabricated with platinum carbonyl complexes on the Pt/C layer is studied for its effect on the power density and stability of the DMFC, the electrochemical surface area (ESA) of the cathode, and impedance of MEAs with a catalyst loading of 1.0 or 2.0 mg(Pt) cm⁻². A DMFC with a conventional cathode based on commercial Pt/C was employed as a reference in order to illustrate the application potentials of the DLC for the reduction of noble metal loading and eventually cost reduction for DMFCs.

2. Experimental

2.1. Materials

All solvents and chemical reagents were used as received. Sodium chloroplatinate (Na₂PtCl₆·6H₂O) was purchased from Alfa Aesar. Sodium acetate (CH₃COONa, AR), methanol (CH₃OH, AR), ethanol (EtOH, AR), and isopropyl alcohol ((CH₃)₂CHOH, AR) were supplied by Sinopharm Chemical Reagent Co., Ltd. Nafion[®] 115 membrane, Nafion[®] solutions (5.3 wt.%), and PTFE solutions (60 wt.%) were purchased from DuPont. Pt–Ru/C (Pt loading: 40%, Ru loading: 20%; HiSpec 10000), Pt–Ru black (atomic ratio 1: 1, HiSpec 6000), Pt black (HiSpec 1000), and Pt/C (Pt loading: 60%, HiSpec 9100) were purchased from Johnson Matthey. Commercial XC-72R carbon black (Cabot), carbon paper (TGPH060, 20 wt.% PTFE, Toray) and 10 wt.% PTFE solution (diluted with the 60 wt.% PTFE solution) were used to prepare gas diffusion layers (GDLs) for DMFCs. Ultrapure water (conductivity 18.2 MΩcm) was used for solution preparation.

2.2. Synthesis of platinum carbonyl complexes

Platinum carbonyl complexes were synthesized using methanol as the solvent by the reaction of Na₂PtCl₆ with CO at 50 °C for 24 h under constant mechanical stirring [23]. NaAc was added to the reaction mixture with a NaAc/Pt molar ratio of 7.2 before the introduction of CO. The as-prepared platinum carbonyl complexes solution was kept in a glove box before use, which yielded a Pt concentration of 32.0 mM by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.3. Pt nanorods formation

Briefly, 2.0 mL platinum carbonyl complexes solution was spread onto a substrate such as a silicon wafer under ambient environment. Methanol was allowed to evaporate at room temperature for 2 h, and the substrate was washed with ultrapure water several times before drying at 50 °C over night for further characterization.

2.4. Membrane electrode assembly (MEA) preparation

Cathode and anode were prepared as follows. Carbon papers coated with a slurry of XC-72R carbon and PTFE (20 wt.%) (1.0 mg cm⁻²) were applied as the anode gas diffusion layers (GDLs) and those with XC-72R carbon (2.0 mg cm⁻²) as the cathode GDLs. For the anode, an ink including commercial Pt–Ru black and

Pt–Ru/C (molar ratio 1:1) with 20 wt.% Nafion[®] was sprayed on the surface of anode GDLs using a Sono-Tek Ultrasonic Atomizing Nozzle System. The metal loading is ca. 4.0 mg(Pt–Ru) cm⁻². For the cathode, conventional single-layered cathode was prepared with the same procedure as the anode except that the catalysts were commercial Pt black and Pt/C (molar ratio 1:1). In this work, the catalyst layer made from commercial Pt black and Pt/C was denoted as the Pt/C layer.

Double-layered cathode (DLC) was prepared by spreading a certain volume of platinum carbonyl complexes solution onto a conventional cathode as fabricated above under ambient environment. The solvent was allowed to evaporate for 2 h in air and subsequently the cathode was washed several times with ultrapure water and dried at 50 °C in an oven over night to yield a DLC. The Pt loading in the first and second layer were kept same (both 0.5 or 1.0 mg(Pt) cm⁻²). The original Nafion solution was diluted with a mixture of isopropanol and water (volume ratio 1:1) by sonication for 2 h yielding a mixed solution containing 1.0 wt.% Nafion[®] ionomer. Then, the Nafion[®] solution was sprayed onto the DLC before MEA fabrication and the Nafion[®] content in the DLC was 20 wt.%.

Nafion[®] 115 membranes were treated according to published procedures before membrane electrode assemblies (MEAs) preparation [8]. MEAs (active-area 1 × 1 cm²) were fabricated by hot-pressing (130 °C, 2 MPa) a pre-treated Nafion[®] 115 membrane sandwiched between an anode and a cathode for 3 min. The MEA was kept in 2.0 M methanol solution before test.

2.5. Characterization

UV–Vis spectra of the platinum carbonyl complexes were collected using a UV–Vis spectrophotometer (Unico 2802). X-ray photoelectron spectra (XPS) were recorded using an X-ray photoelectron spectroscopy (Kratos AXIS UltraDLD, Britain) with Al Kα radiation. The binding energies derived from XPS measurements were referenced to the C1s binding energy at 284.45 eV. X-ray diffraction (XRD) measurements were conducted using a Bruker AXS D8 Advance powder X-ray diffractometer with Cu Kα 1 radiation (λ = 0.15406 nm). The tube voltage was maintained at 40 kV, and the tube current at 100 mA. All of the data were collected at a scanning rate of 2° min⁻¹ with a step size of 0.02°. Transmission electron microscopy (TEM) images, high resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) data were collected on a JEOL 2100F at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) micrographs were scanned at an electron acceleration voltage of 10.0 kV (S-4800 FE-SEM, Hitachi). Composition of the catalyst from platinum carbonyl complexes was detected on IRIS advantage ICP-AES system (Thermo America).

2.6. Electrochemical characterization

Polarization curves of the passive DMFCs, fed with 2.0 M methanol (5 ml), were obtained on an Arbin FCT testing system (Arbin Instrument Inc. USA) in an air-breathing mode for each discharging current point along the polarization curve. The stability of the DMFC was tested at a constant current density of 40 mA cm⁻² for 120 h with methanol solution replacement at about every 12 h. Anode polarizations were measured by an M273A Potentiostat/Galvanostat (EG&G, PAR). The anode fed with 2.0 M methanol (5 ml) was served as the working electrode, and the cathode with humidified H₂ was applied as the counter electrode and reference electrode.

Cyclic voltammograms were recorded at a scan rate of 20 mV s⁻¹ between 0.05 and 0.75 V using a Solartron SI 1287 Electrochemical Interface setup. The cathode fed with humidified N₂ was denoted as

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