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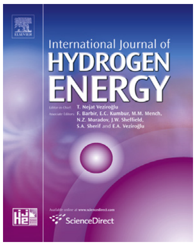

Short Communication

Highly stable Ti–Co–Phen/C catalyst as the cathode for proton exchange membrane fuel cells

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ABSTRACT

A Ti–Co–Phen/C catalyst was prepared for polymer electrolyte membrane fuel cells (PEMFCs) without precious metals using a modified polymer complex (PC) method with 1,10-phenanthroline (Phen) as the nitrogen precursor. The oxygen reduction reaction (ORR) activity of the Ti–Co–Phen/C catalyst was significantly higher than the ORR activity of the Ti–Co/C catalyst prepared with the PC method because the former had a larger N surface content due to its highly dispersed Co species. The catalyst also exhibited excellent chemical stability in acidic media due to the probable strong interactions between the highly dispersed Ti and Co species. A H_2/O_2 PEMFC using the Ti–Co–Phen/C catalyst as the cathode demonstrated excellent cell performance. A 0.68 W cm^{-2} maximum power density was obtained. The cell performance stability did not drop perceptibly during its 550-h lifetime at 0.5 V and its 300-h lifetime at 0.7 V. The prepared Ti–Co–Phen/C catalyst exhibited both high ORR activity and excellent performance stability, making it a promising alternative for the cathode catalysts in PEMFCs.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are a promising power source because they provide high energy conversion efficiency and low emissions [1–3]. However, Pt-based cathode catalysts are too expensive for widespread use in commercialised PEMFCs [4,5]. Significant efforts over the last several decades have focused on developing non-precious metal cathode catalysts for PEMFCs. Recently, several breakthroughs have been reported that non-precious metal catalysts have demonstrated a significant increase in performance, allowing them to compete with the Pt-based catalysts [6–11]. Currently, the polyaniline FeCo–C catalyst [10] is the most promising catalyst because it combines high oxygen reduction reaction (ORR) activity with good performance stability relative to other non-precious metal catalysts.

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A 0.55 W cm^{-2} peak power density was observed at 0.38 V in a pure oxygen atmosphere. More importantly, a H_2/air fuel cell prepared with this catalyst exhibited a 0.4 V-current density over the course of a 700 h stability test without any obvious degradation. However, PEMFCs operating below 0.6 V are not practical for industrial applications because the efficiency of converting the chemical energy (H_2) into electrical energy is proportional to the fuel cell voltage [12,13]. Therefore, when evaluating a cathodic catalyst in PEMFCs, a high ORR activity and excellent performance stability in cells must occur above 0.6 V. Recently, a Co-PPY-C composite catalyst [7] exhibited high ORR activity. Unfortunately, when the cell performance stability of this catalyst was evaluated at 0.5, 0.6 and 0.7 V, the cell lifetime were uniformly less than 100 h. Therefore, for non-precious metal catalysts to become commercially viable, their performance stability in PEMFCs at high voltages must be improved.

In our previous work, we prepared a Ti–Co–O–N/C catalyst [14] using the polymer complex (PC) method and later performed a nitridation under flowing ammonia at 900 °C for 5 h. This catalyst exhibited excellent chemical stability in acidic media because the Ti and Co species interacted strongly with one another. However, the ORR activity of the Ti–Co–O–N/C catalyst was not as high as the reported non-precious metal catalysts'ORR activity. Although highly dispersed metal ions in the catalyst can be obtained when using the PC method because the contact between the metal ions and carbon black is ensured [14–16], the N content on the surface of the catalysts was notably low after the high-temperature nitridation under an ammonia atmosphere, generating a relative low ORR activity. In this work, a Ti–Co–Phen/C catalyst was prepared using a modified PC protocol using 1,10-phenanthroline (Phen) as the nitrogen precursor followed by a 5-min nitridation reaction. The prepared catalyst exhibited significantly higher ORR activity than that of the Ti–Co/C catalyst prepared using the PC method and a 5-h nitridation. Specifically, the PEMFC incorporating Ti–Co–Phen/C as the cathode catalyst exhibited improved performance stability at 0.5 V and 0.7 V.

Experimental

The Ti–Co–Phen/C catalyst was prepared using a modified PC method followed by a 5-min nitridation at 950 °C under flowing ammonia. The preparation process proceeded as follows: 1.002 g $TiCl_4$ (99.0%, Sigma–Aldrich) and 0.251 g $CoCl_26H_2O$ (99.0%, Sigma–Aldrich) were dissolved in 100 mL methanol with vigorous stirring. Subsequently, 6.050 g citric acid (CA, 99.5%, Sigma–Aldrich) and 7.819 g ethylene glycol (EG, 99.5%, Sigma–Aldrich) were added to the solution. The molar ratio of the raw materials was Ti:Co:CA:EG = 5:1:30:120. The resulting mixture was concentrated and polymerised at 150 °C until gelation was attained. 5.000 g Carbon black (Vulcan XC-72R, Cabot Corp.), 1.768 g 1,10-phenanthroline (Phen, 99%, Sigma–Aldrich) and 250 mL methanol were added to the gel. The flask was heated to 200 °C to obtain the precursor powder. The mass ratio between Phen and carbon black was 35:100. The precursor powder (3 g) was heated in an NH_3 atmosphere (flow rate of 300 mL min^{-1}). The temperature was increased from room temperature to 950 °C at 10 °C min^{-1} and subsequently held for 5 min. After cooling to room temperature, the as-synthesised sample was immersed in an 80 °C 0.5 M H_2SO_4 solution for 24 h under atmospheric conditions to eliminate any unstable metal species and subsequently filtered. After drying, a Ti–Co–Phen/C catalyst was obtained, and the Ti loading was calculated to 5.0 wt.%.

The Ti–Co/C catalyst was prepared using the PC method and a subsequent high-temperature nitridation under flowing ammonia for 5 h, as described previously [14]. Briefly, 1.002 g $TiCl_4$ (99.0%, Sigma–Aldrich) and 0.251 g $CoCl_26H_2O$ (99.0%, Sigma–Aldrich) were dissolved in 100 mL methanol with vigorous stirring. Subsequently, 6.050 g citric acid (CA, 99.5%, Sigma–Aldrich) and 7.819 g ethylene glycol (EG, 99.5%, Sigma–Aldrich) were added. The molar ratio of these raw materials was Ti:Co:CA:EG = 5:1:30:120. The resulting mixture was concentrated and polymerised at 150 °C until gelation was achieved. 5.000 g Carbon black (Vulcan XC-72R, Cabot Corp.) and 250 mL methanol were added to the gel and heated to obtain the precursor powder. The precursor powder (3 g) was heated under an NH_3 atmosphere (flow rate of 300 mL min^{-1}). The temperature was increased from room temperature to 950 °C at 10 °C min^{-1} and subsequently held at 950 °C for 5 h. During the nitridation, the weight loss of the samples was ~40 wt.%. After cooling to room temperature, the as-synthesised sample was immersed in an 80 °C 0.5 M H_2SO_4 solution for 24 h under atmospheric conditions to eliminate any unstable metal species and subsequently filtered. After drying, a Ti–Co/C catalyst was obtained, and the Ti loading was calculated to 5.0 wt.%.

X-ray diffraction (XRD) was performed using a Rigaku D/Max 2500 V/PC diffractometer to study the crystal structure of the catalysts. X-ray photoelectron spectroscopy (XPS) measurements were performed on a JPS-90SX, JEOL to analyse the surface compositions and properties of the catalysts. Mg K was used as the excitation radiation at a constant pass energy of 20 eV. The electron binding energy was referenced to Au 4f 7/2 at 83.8 eV and the C 1s peak at 284.6 eV.

The working electrodes were prepared as follows: 5 mg catalyst, 1 mL ethanol and 50 μL Nafion solution (5 wt%, Sigma–Aldrich) were mixed and ultrasonicated for 30 min to form a catalyst ink. A 30 μL aliquot of the ink was placed on 1 cm^2 carbon paper (TGP-H-120, Toray) and dried at 80 °C in air. A conventional three-electrode electrochemical cell was used to assess the ORR activity. A Pt wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The Ag/AgCl reference electrode was calibrated against the reversible hydrogen electrode (RHE) potential of 101 kPa for H_2 in a 0.1 M aqueous H_2SO_4. Before performing the ORR measurements, the electrode was repeatedly polarised between 0.11 and 1.20 V to achieve a stable profile in the cyclic voltammogram (CV). The electrochemical activity for the ORR was determined using a linear scan voltammogram (LSV) from 1.20 to 0.11 V at a 5 mV s^{-1} sweep rate in an O_2-saturated 0.1 M H_2SO_4 aqueous solution. The ORR current was corrected for the background current. The background current was obtained by saturating the 0.1 M H_2SO_4 aqueous solution with N_2 gas and performing a linear sweep scan.

A membrane-electrode-assembly (MEA) was prepared using Ti–Co–Phen/C as the cathode. The cathodic catalyst ink