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Tuning the oxygen reduction reactivity of interconnected porous carbon by incorporation of phosphorus and activity enhancement through blending with 2D metal dichalcogenides materials

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ABSTRACT

Design and construction of strong oxygen reduction reaction (ORR) electrocatalysts with high activity and durability are the main concerns in proton exchange membrane fuel cells (PEMFCs). In this study, a unique interconnected porous carbon (ICPC) and phosphorus doped ICPC (P-ICPC) were synthesized and utilized as a support matrix for ORR in alkaline medium. The activity of P-ICPC further enhanced by compositing with 2D metal dichalcogenide MoS_2 materials through facile hydrothermal method. The structural characterization indicated that the addition of phosphorus created more defective site in the carbon structure. The MoS_2/P-ICPC catalyst exhibited enhanced ORR activity, and its performance is close to commercial Pt/C catalyst with regards to current density and onset potential. The synthesized MoS_2/P-ICPC catalyst shows better stability regarding activity even after the 2000 cycles of acceleration test. The electron transfer number (n) obtained for MoS_2/P-ICPC is ~3.8, indicating that the oxygen reduction reaction proceeds via $4e^-$ pathway with the similar kinetics of commercial Pt/C. The current results revealed that the synthesized MoS_2/P-ICPC material might be a better catalyst for oxygen reduction reaction.

Introduction

Fuel cell development has attracted tremendous attention during the last few decades because it is considered as a clean and efficient power source to replace the traditional energy [1,2]. The cathode oxygen reduction reaction (ORR) is a crucial step that determines the performance of fuel cells [3,4] and Pt, Pt-based materials most commonly used as catalyst materials for ORR [5]. The unique, precious metal structures such as Pt-based alloys [6], core-shell structure [7], nanoflower [8] and nanowires [9,10] have been successfully designed and demonstrated for ORR reactions and compared with the traditional commercial Pt/C catalyst. However, several disadvantages including kinetically slow ORR processes, methanol crossover, and expensive Pt catalysts, hinder the mass

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production of these devices. So, it is vital to develop robust non-Pt catalysts to catalyze ORR [11–14]. Until now, unflagging efforts have taken into the development of efficient ORR catalysts, including heteroatom-doped carbon [15–17], and non-precious metals [18,19] as electrocatalysts. The heteroatom (N, S, and P) doped carbon materials showed improved ORR activities than individual carbon materials. Many research outputs revealed that the formation of defect sites on the carbon surface by doping leads to increased adsorption of O_2 species, react at a faster rate and produce more activity. Incorporation of N on the carbon structure causes modification of the electronic structure of carbon due to the large electronegativity of N, which favors the absorption of O_2 and further increase the ORR [20,21]. Recently, phosphorus doped cylindrical mesoporous carbon derived from silica SBA-15 was tested for ORR and found that the incorporation of phosphorus creates defective sites for O_2 adsorption, and the available electron pair on phosphorus enhances asymmetric spin density in the adjacent carbon atom. Also, the channel length of mesoporous carbon plays a significant role in the enhancement of ORR activities [22]. Similarly, transitional metal sulfides such as nanometer-scaled MoS_2 and WS_2 have attracted considerable attention recently as inorganic electrocatalysts because of their low cost, chemical stability and excellent electrocatalytic properties [23,24]. Bulk MoS_2 is a poor electrocatalyst [25], but, nanocrystals of MoS_2 and related metal sulfides are more active [26–28] towards various chemical reactions. Therefore, considerable efforts have been made to design the MoS_2 catalyst for excellent ORR activity in this study. For improving the electrocatalytic activity of MoS_2, three strategies are in practice (i) increasing the intrinsic activity of active sites, (ii) improving the electrical contact to these sites and (iii) increasing the number of defect sites [29]. Highly conductive materials, including carbon [30], reduced graphene oxide [31], carbon nanotubes [32], and carbon nanospheres [33] were used to improve the electrical contact. Interestingly, doping of phosphorus on MoS_2 found to improve the ORR characteristics due to electronegativity difference between P and MoS_2 [34]. The interconnected mesoporous carbon (ICPC) was derived from silica KIT-6 (Korea Advanced Institute of Science and Technology, number 6) [35]. These ICPC materials were doped with phosphorus through high-temperature pyrolysis protocols and further encapsulated with MoS_2via hydrothermal method. The morphological and structural properties were characterized using TEM, SEM, XRD, Raman and XPS analysis. The electrochemical ORR activity, durability and methanol tolerance of MoS_2/P-ICPC materials were studied and compared with Pt/C catalyst in alkaline medium.

Experimental section

Materials

All the chemicals such as tetraethyl orthosilicate (TEOS), block copolymer P123, 1-butanol, hydrochloric acid, sucrose, sulfuric acid, triphenylphosphine (TPP), sodium molybdate, thiourea, and polyethylene glycol (PEG) purchased from Merck or Sigma-Aldrich and used as received without further purification. All solutions used for electrocatalytic studies were prepared using Milli-Q (18.2 MΩ cm) water.

Synthesis of mesoporous silica and P-doped carbon (P-ICPC)

Mesoporous silica KIT-6 was synthesized using the following procedure [36]. Typically, 2.25 g pluronic P123 block copolymer was dissolved in 82 g of deionized water and 4.35 g of 37 wt% HCl. Then, 2.25 g of butanol added with vigorous stirring followed by 4.9 g of TEOS to the solution while stirring. The mixture was left under constant stirring for 24 h at 35 °C and hydrothermally treated at 100 °C for 24 h in a Teflon-lined autoclave. The resulted solid product was filtered and dried at 100 °C for 12 h, and template removal was done by calcination of the materials at 550 °C for 8 h. Phosphorus doped carbon materials synthesized using the following procedure [22]. Typically 250 mg of KIT-6 silica was mixed with 25 mg of TPP and 5 ml of phenol; the resulted mixture stirred at room temperature. Later, the obtained mixture was dried at 80 °C overnight at vacuum followed by carbonization at 900 °C in an inert atmosphere for 5 h. Finally, the silica removal was carried out using HF treatment [37].

Synthesis of MoS_2/P-ICPC catalyst

For the preparation of MoS_2/P-ICPC materials, the calculated quantity of precursor's salts (0.08 g Na_2MoO_4, 0.1 g of thiourea, 0.013 g PEG and 10 ml of H_2O) mixed with previously synthesized 0.1 g P-ICPC support and stirred for 12 h at room temperature. The mixture was transferred to Teflon-lined stainless steel autoclave and heated to 180 °C for 24 h. The obtained product was washed and dried at 60 °C in vacuum condition.

Physical characterization

The structural properties of the synthesized materials characterized by X-ray diffractometer (Bede Scientific Ltd., UK; Cu Kα radiation; operated at 40 kV). In XRD analysis, diffraction angle measured ranging from 10 to 80°, with a step rate of 3° min^{-1}. Laser Raman analysis was carried out using Renishaw Invia Raman Microscope. Surface morphology of these materials examined by FESEM, ZEEIS X-Max Oxford Instruments and Tecnai G20 TEM operating at 200 kV. The physical properties were studied using X-ray photoelectron spectroscopy (XPS). Multilab 2000 Thermo scientific (UK) X-ray photoelectron spectrometer used for the analysis. Mg Kα X-ray (1253.6 eV) with 200 W power used as the exciting source and 10 eV energy pass used for data collection. The energy analyzer employed was a hemispherical analyzer of 150 mm diameter. The vacuum maintained during the experiment was 10^{-10} mbar. Experimental data were curve fitted using Shirley Background with a Gaussian and Lorentzian mix product function.

Electrochemical studies

The electrochemical performances of the prepared catalysts characterized by linear sweep voltammetry (LSV) using a

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