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Ternary non-noble metal chalcogenide (W–Co–Se) as electrocatalyst for oxygen reduction reaction

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Abstract

In this study, a catalyst based on a novel ternary non-noble metal chalcogenide, W–Co–Se, was synthesized for the oxygen reduction reaction (ORR) in acidic medium. The non-noble metal chalcogenide catalyst was electrochemically stable in the potential range of 0.05–0.8 V versus NHE in 0.5 M H_2SO_4 aqueous solution. This catalyst demonstrated significant catalytic activity towards the ORR, showing the ORR onset potential at 0.755 V versus NHE in 0.5 M H_2SO_4 at 25 °C. Such high activity might be attributed to the electronic structure of non-noble metals modified by chalcogen.

Keywords: Oxygen reduction reaction (ORR); Non-noble metal catalyst; Chalcogenide; Polymer electrolyte fuel cell (PEM)

1. Introduction

In the effort to reduce the cost and improve the reliability of platinum (Pt)-based fuel cell catalysts [1,2], a non-Pt catalysis approach has attracted great attention over last several decades [3,4]. Among the non-Pt catalysts explored, the ruthenium (Ru)-based chalcogenide catalysts synthesized by Alonso-Vante et al. [5,6] have been among the most promising, due to their high activity and stability towards the oxygen reduction reaction (ORR) in acidic media. With respect to non-Ru chalcogenides, which are non-noble catalysts, Behret et al. [7] synthesized several cobalt (Co)-based catalysts such as Co_3S_4. Recently, Susac et al. [8] showed that a cobalt–selenium (Co–Se) chalcogenide catalyst prepared by sputtering and chemical methods was also catalytically active towards the ORR in an acidic medium. Sidik and Anderson [9], using slab and quantum computational approaches, proved that the partially OH-covered (202) surface of a Co_9S_8 chalcogenide is an active site for ORR. In terms of the ORR overpotential, this surface has a similar behavior to that of a Pt surface. These studies are encouraging for the further improvement in the catalytic activity of such non-noble metal chalcogenides, which normally have lower ORR catalytic activity than do Ru-based chalcogenide catalysts.

In the continuing effort to improve ORR catalytic activity, this work synthesizes a novel ternary non-noble metal chalcogenide based on tungsten (W) and Co. Although these two non-noble metals are inactive towards the ORR and unstable in an acidic medium, it can be expected that the electronic structures modified by a chalcogen such as Se might enhance their stability and activity [10]. The ORR catalytic activity and the stability of the synthesized W–Co–Se chalcogenide were evaluated in an acidic medium. The relationship between the modified electronic structures and the corresponding catalytic activity was explored.

2. Experimental

2.1. Synthesis

The W–Co–Se chalcogenide catalyst was synthesized by chemical precipitation reaction among tungsten carbonyl (Tungsten hexacarbonyl: $W(CO)_6$, 99.9+%, Aldrich, 239 mg), cobalt carbonyl (Dodecacarbonyltetracobalt:

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$Co_4(CO)_{12}$, 98.0+%, Alfa Acesar, 97 mg) and selenium (200 mesh power, 99.999%, Alfa Acesar, 54 mg) in 300 mL of xylene (98.5+%, Alfa Acesar) solvent [11]. The xylene solvent was bubbled with argon for over 30 min to remove dissolved oxygen before the selenium powder was added. Then the xylene reflux was heated to 140 °C for 30 min and cooled to room temperature. The tungsten and cobalt carbonyls were added to this xylene reflux, which was then heated to 140 °C. After being heated for over 20 h, the reflux was cooled and the precipitates were filtered and then washed with diethylether (99%, Alfa Acesar). All of the procedures were performed under argon with stirring.

2.2. Instrument characterization of the catalysts

The morphology and particle size of the synthesized samples were characterized using a transmission electron microscope (TEM, Hitachi H-1600). The microstructure was confirmed by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer in Bragg-Brentano configuration) with Cu Kα radiation. The XRD patterns were recorded between 10° and 90° at a step time of 1.5 s per 0.02°. The samples were adhered onto the glass with Vaseline and the sample holder was rotated during the data collection to improve particle statistics. The powder diffraction file database from the International Centre for Diffraction Data was used as a reference to interpret peak assignments on the XRD patterns.

The surface characterization of the synthesized sample was conducted by X-ray photoelectron spectroscopy (XPS, Leybold MAX 200 XPS Spectrometer) using Al Kα radiation. The electron binding energy of the XPS was referenced to Au $4f_{7/2}$ at 84 eV and C 1s of a carbon contamination at 285 eV [12,13]. The average chemical compositions for surface and bulk were determined by XPS and energy dispersive X-ray (EDX, Hitachi S3500N with EDX) analysis, respectively.

2.3. Electrode preparation and electrochemical measurements

The catalyst ink, a well-mixed suspension of the synthesized W–Co–Se chalcogenide powder and deionized water, consisted of 8.88 mg mL^{-1} of catalyst. For the electrode coating process, a 5 μL of catalyst ink and a 5 μL of diluted Nation® solution (as-received 5 wt% Nafion® from Sigma–Aldrich was diluted with deionized water to 0.05 wt%) were pipetted onto the glassy carbon (GC) disk electrode (geometric area of 0.164 cm^2), and the coated electrode was left in the air to dry. The catalyst loading coated on the glassy carbon electrode was 270 μg cm^{-2}. For comparison, 122 μg cm^{-2} of Pt/C catalyst (40 wt%, E-TEK, Pt loading: 48.8 μgcm^{-2}) was coated on the electrode surface in the same way.

The electrochemical characterization for the prepared electrode was performed in a conventional electrochemical cell with a three-electrode configuration using a rotating disk technique. A KCl saturated calomel electrode (SCE, $E^{o}_{SCE} = 0.241$ V versus NHE at 25 °C) and Pt wire were used as the reference and the counter electrodes, respectively. A 0.5 M H_2SO_4 aqueous solution was used as the electrolyte. All the tests were conducted at 25 °C under 99.999% oxygen and nitrogen bubbling. All reported electrode potentials were expressed versus normal hydrogen electrode (NHE). The cyclic voltammetry was carried out in the range of 0.05–0.8 V versus NHE at a potential scan rate of 50 mV s^{-1}. The slow scanning voltammetry was recorded at a potential scan rate of 5 mV s^{-1} between 0.8 and 0.05 V versus NHE. All reported current densities were normalized to the geometric surface area of the disk electrode.

3. Results and discussion

The average chemical composition ratios for the surface and the bulk of the synthesized W–Co–Se chalcogenide powder were determined by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX) analysis. Table 1 shows the average composition ratio for the surface and the bulk of W–Co–Se chalcogenide. The surface of the synthesized sample was tungsten-rich compared to the bulk. It is worthwhile to note that no noble metal contamination was found either on the surface or in the bulk of the sample.

Fig. 1 shows the micrograph and the diffraction pattern of the W–Co–Se sample, taken by transmission electron

Table 1
Chemical composition ratio (at.%) for surface and bulk of W–Co–Se chalcogenide

	W	Co	Se
Surface (XPS analysis)	30.0	37.5	32.5
Bulk (EDX analysis)	11.3	42.4	46.3

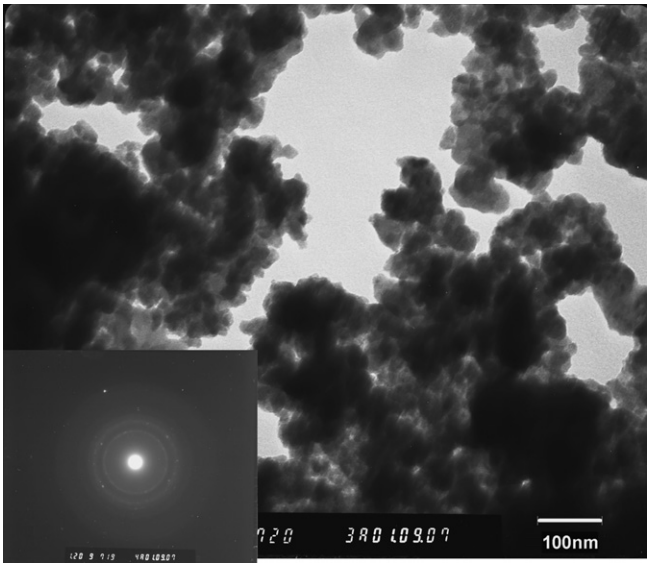

Fig. 1. TEM micrograph and diffraction pattern for W–Co–Se.