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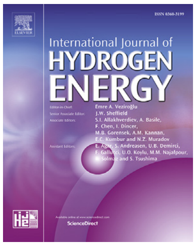

One-pot hydrothermal synthesis of supported CoS electrocatalysts: The effect of support nature on oxygen reduction reaction activity in alkaline medium

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ABSTRACT

The development of efficient and durable earth-abundant electrocatalysts for the oxygen reduction reaction (ORR) is an ongoing challenge. In this work, we directly anchored CoS nanocatalysts (20 wt%) on different supports, namely, carbon nanotubes (CNTs) and reduced graphene oxide by a single-pot hydrothermal route. The developed synthesis processes enabled us to alter the composite nature of CoS by changing the sulfur precursor used. The corresponding electrocatalytic performance of these composite catalysts toward the ORR was studied in alkaline medium. The increase in the effective electrode surface area that accompanies the CoS nanocomposite substantially boosts its ORR catalytic performance. The CoS-CNT-Cy hybrid material shows an onset potential of 0.85 V, which is 60–200 mV less negative than that of other catalysts tested. The catalytic current density achieved with the hybrid material at 0.2 mg cm^{-2} is comparable with that of commercial Pt/C (20%). The synergistic effect of CNTs and CoS enhances the overall performance of the hybrid catalyst. Extension of this nanocomposite strategy to other earth-abundant materials could similarly enable inexpensive electrocatalysts that lack the high intrinsic activity of the noble metals.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are believedto be one of the alternative power supplies for stationary, transportation, and portable applications. However, the high cost of noble-metal catalysts and perfluorinated membranes as well as the relatively short durability of the catalyst materials severely hinder wide-scale commercialization of PEMFC systems [1,2]. In comparison with PEMFCs, alkaline fuel cells (AFCs) use non−noble metal catalysts (e.g., Ag, Ni, or metal oxides). Most catalyst materials have higher stability in this medium [3]. In comparison with PEMFCs, AFC systems have been less investigated with respect to catalyst materials and alternate polymer membranes [4]. In the recent past, some promising alkaline polymer electrolytes, such as quaternary ammonia polysulfone [5–7] and a polyethyleneco-tetrafluoroethylene–based polymer [8], have been developed. It is

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true that these novel alkaline anion-exchange membranes have stimulated the development of alkaline membrane fuel cells which have, in turn, attracted further interest [9].

A major limiting factor of energy conversion efficiency for present fuel cells is the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode. Even though non-precious metal–based alternative electrocatalysts have been identified for this purpose, they still lack long-term stability. Transition metal chalcogenides as potential ORR catalysts for fuel cells have received more attention since Alonso-Vante et al. [10] reported for the first time the significant catalytic activity of the Chevrel-phase Mo_6Se_8 toward the ORR in acidic medium [11–13]. The cathodic oxygen reduction in chalcogenides of various transition metals has been further reported [14–19]. In recent reports, $CoSe_2$ has been studied as a non–precious metal chalcogenide catalyst in acid [20] and alkaline [21] conditions. Cobalt sulfides have been investigated as ORR catalysts with the highest activity among all chalcogenides of nonprecious metals in alkaline solution [22].

Recently, Liu et al. demonstrated [23] a novel graphene-coated/Co_9S_8 nanoparticle–embedded nitrogen-doped porous carbon dodecahedron hybrid (Co_9S_8/NPCP@rGO) prepared by the pyrolysis and sulfuration of precursors composed of graphene oxide and zeolitic imidazolate frameworks (ZIFs). The Co_9S_8/NPCP@rGO hybrid is used as a highly efficient non–precious metal electrocatalyst for oxygen reduction and exhibits more positive onset potential and half-wave potential, higher limiting current density, lower Tafel slope, and better durability and methanol tolerance in alkaline media in comparison to the commercial 20 wt% Pt/C catalyst. An independent work reported by Bai et al. [24] evaluates the porous carbon-coated $CoS_{1.097}$ nanocomposites (PC-$CoS_{1.097}$NCs) synthesized by a one-step controlled pyrolysis of the zeolitic imidazolate framework ZIF-9 with sulfur powder. The resulting porous composites contained a high level of nanoparticles of $CoS_{1.097}$ and exhibited considerable mesoporosity. With remarkable electrocatalytic activity, the nanocomposites provided a four-electron pathway for the ORR in alkaline medium.

In a similar attempt, Ganesan et al. [25] presented a simple approach for the preparation of cobalt sulfide nanoparticles in situ grown on a nitrogen and sulfur–codoped graphene oxide surface. The particle size and phase were controlled by changing the treatment temperature. Cobalt sulfide nanoparticles dispersed on graphene oxide hybrids were successfully prepared by a solid-state thermolysis approach at different temperatures using cobalt thiourea and graphene oxide. X-ray diffraction (XRD) studies revealed that hybrids prepared at 400 and 500 °C result in a pure CoS_2 phase, whereas the hybrid prepared at 600 °C exhibits a Co_9S_8 phase. X-ray photoelectron spectroscopy (XPS) studies revealed that nitrogen and sulfur simultaneously codoped on the graphene oxide surface, and these sites act to anchor the CoS_2 nanoparticles strongly on the GO surface. The strong coupling between CoS_2 and N,S-GO was reflected in the improvement of the oxygen electrode potential. CoS_2(400)/N,S-GO showed outstanding oxygen electrode activity with a potential of about 0.82 V against a reversible hydrogen electrode in alkaline medium. A recent report by Cao et al. [26] demonstrated Co_9S_8 embedded in porous nitrogen-doped carbon (N-C) matrix by designing an ion exchange and doping process. The as-fabricated Co_9S_8/N-C hybrid shows excellent ORR activity, which is comparable with that of the commercial Pt catalyst.

Even though current ORR catalysts based on cobalt sulfides have exhibited activity equal to that of Pt, it has been shown that two-electron reduction is the dominant reaction pathway for cobalt sulfide catalysts [27]. Moreover, a detailed study on the effect of carbon supports such as carbon nanotubes (CNTs) and reduced graphene oxide (rGO) on cobalt sulfide catalyst activity has gone unreported. In addition, it is highly desirable to design and synthesize high-performance cobalt sulfide–based electrocatalyst materials capable of catalyzing a four-electron pathway toward the ORR. It has been proved earlier that the combination of commercially available carbon allotropes and their derivatives with transition metal oxide materials enhances the electronic conductivity of the composites and also prevents agglomeration of metal oxide nanoparticles during continuous electrochemical tests [28–30].

In the present study, we describe a facile route to obtain cobalt sulfide CNTs and cobalt sulfide–rGO hybrid electrocatalysts from various sulfur precursors. The method follows a controlled single-step hydrothermal synthesis protocol for CoS nanoparticle (20 wt%) decoration on these supports. Measurements with a rotating ring disc electrode (RRDE) showed that a nearly four-electron ORR can be achieved with the CoS-CNT-Cy hybrid catalyst in 0.1 M KOH. The CoS-CNT-Cy hybrid material is the best catalyst for the ORR among all cobalt chalcogenide–based materials investigated in the present work.

Experimental

Chemicals used

Cobalt(II)nitrate hexahydrate, cobalt(II)chloride hexahydrate, thioacetamide, carbon disulfide, L-cysteine, sodium sulfide, and ethanol were obtained from Merck. Thiourea, polyvinyl pyrrolidone (PVP), and Nafion were obtained from Aldrich. Cetyl trimethyl ammonium bromide (CTAB) and MWCNTs purchased from SRL with 95% purity, 10–30 μm length, and >50 nm diameter were used in this study. Graphene oxide and potassium hydroxide were obtained from Fisher. All the chemicals used were of analytical grade and used as received. Milli-Q ultrapure water was used to prepare all the solutions.

Purification of MWCNTs

Before the synthesis of electrocatalysts, MWCNTs were purified by the following procedure to avoid the presence of any trace metals: Initially, 1 gm of MWCNTs was dispersed in 350 ml of 6 M HNO_3 solution and heated to 110 °C for 48 h. Then, the solution was filtered and washed several times with DI water and ethanol. Finally, the samples were dried using a vacuum oven overnight [31].

Synthesis of CoS-CNT catalysts

Preparation of CoS-CNTs by using thioacetamide (CoS-CNT-TA)

In a typical synthesis process, 100 mg of CNTs was dispersed in 50 ml DI water and sonicated for 1 h [32]. Later, 1.16 g of

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