Molybdenum phosphide-graphite nanomaterials for efficient electrocatalytic hydrogen production

S.S. Jyothirmayee Aravind, Kandalam Ramanujachary, Amos Mugweru, Timothy D. Vaden *

Department of Chemistry and Biochemistry, Rowan University, 201 Mullica Hill Road, Glassboro, NJ 08028, USA

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ABSTRACT

Clean hydrogen energy technology is an alternative to a fossil fuel-based energy economy. Efficient and economical catalysts are necessary for large-scale hydrogen generation. We report MoP and MoP-graphite nanosheets prepared by ball milling commercial compounds as efficient electrocatalytic materials for hydrogen generation via the hydrogen reduction mechanism. The hydrogen generated through electrochemical catalysis was evaluated using gas chromatography. The effects of ball milling time and proportions of MoP-graphite nanosheets on electrocatalytic activity were investigated. The new nanomaterials were characterized using powder XRD, SEM and BET surface area measurements. The results suggest superior electrocatalytic performance with a balance of ball-milled MoP and graphite. A Tafel slope of 63 mV/dec was obtained for this new material.

1. Introduction

Electrocatalytic hydrogen generation is a promising area of research aimed to support the development of a robust hydrogen-based energy economy. Hydrogen can be generated via reduction of hydronium ions on electrode surface. This hydrogen evolution reaction (HER) requires a high overpotential. Currently, platinum-based catalysts offer the best performance for lowering the HER overpotential [1,2]. The high cost and low earth abundance of Pt and Pt group metals hinder their use and present an economic obstacle to widespread application. Therefore, significant research effort has been focused on finding cheap, efficient HER catalytic materials.

Transition metal phosphides are important due to their advanced catalytic and electronic applications. Stinner et al. [3] investigated a series of transition metal phosphides for hydrodenitrogenation and found that MoP is an active catalyst for this application. Recently, it was established that most of the hydrodesulfurization (HDS) catalysts can be good HER catalysts as well. For instance, MoS_2, a well-known HDS catalyst, was investigated for hydrogen evolution reaction. It was found that the HER activity of MoS_2 stems from the more active edge sites rather than the stable basal planes [4]. Based on this fact, and the evaluation of HER activity by DFT on transition metal phosphides, Ni_2P was

identified as a good HER catalyst material [5]. The same group evaluated the HER activity of cobalt phosphide recently [6].

In contrast to the extensive research on sulfides, research on transition metal phosphide HER catalysis is relatively new. Several recent reports have demonstrated the electrocatalytic HER activity of molybdenum phosphide (MoP) materials [7–10]. In the present contribution, we report the effect of particle size and electrochemical synergy between molybdenum phosphide and graphite materials towards HER electrocatalysis. The effects of reduction in particle size in electrocatalytic applications especially in the fields of fuel cells have been investigated [11]. Improved performance due to reduced particle size has been observed due to the enhanced surface area and reactivity at the nanoscale [12]. Nanomaterials are increasingly utilized in the field of clean hydrogen energy technology. Silver nanoparticles coated on TiO_2 nanosheet films are reported to exhibit improved photo-catalytic production of hydrogen than pure TiO_2 nanosheet films [13]. Nanoclusters of Pt, Ru and Rh also exhibit high activities and also generate stoichiometric amount of hydrogen [14]. In order to be useful as an HER catalyst, bulk MoP materials must be doped and ground to reduce the size.

In the current work, we utilize mechanical ball milling technique to reduce the MoP particle size and synthesize MoP nanoparticles for increased HER activity. In the process of ball milling, moving balls apply their kinetic energy to the material thereby breaking inter- and intra-particulate interactions and producing fresh surfaces by fracturing the material particles. The uncompensated bonds on the newly formed surfaces are normally chemically

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* Corresponding author. Tel.: +1-856-256-5457.
E-mail address: vadent@rowan.edu (T.D. Vaden).

reactive. In the literature, ball milling has been reported as a mechano-chemical synthesis method for the production of unique nanostructures with new chemical properties. Large-scale synthesis of nitrogen-doped carbon nanomaterials have been prepared by ball milling followed by annealing for electrochemical applications [15]. Wang et al. [16] utilized high energy ball milling to convert commercial microcrystalline MoS_2 into distorted MoS_2 nanostructures and report improved HER catalytic performance. Hence it is clear that reducing the particle size favorably affects the HER activity. A detailed characterization of MoP compounds along with their electrochemical studies is reported in the present work.

Ball-milled MoP particles are at a risk of agglomeration due to high surface area. Incorporating high surface area materials such as graphite can help in the preparation of highly dispersed MoP nanoparticles. Graphite has garnered wide interest in the last few years due to its unusual combination of properties arising from the high degree of anisotropy that has been attributed to its hexagonal crystal structure. Graphite nanoparticles and nanosheets have been utilized as electrodes in lithium recharged batteries [17], adsorption substrates [18], and as a reinforcing material in nanocomposites [19], and they can be produced by chemical or mechanical methods. The most common experimental method to produce graphite nanosheets [20] or graphene nanoplatelets [21] is mechanical milling. The milling process brings about structural transformations in graphite and generates different defects [20], which can be exploited to anchor nanoparticles towards graphite planes. Ball milling has also been investigated as an alternative process to enhance the adhesion between Polyetherimide and exfoliated graphite nanoplatelets particles and also to reduce the particle size. High electrical conductivity and enhancement in modulus are achieved by this approach along with improved strength properties [22]. The performance of electrocatalytic materials can be further improved by the synergetic combination of electrocatalytic components, often by the use of carbon nanomaterials for superior conductivity and simplified substrate architecture. The electrical coupling between MoS_2 nanoparticles and graphene is found to improve the electrocatalytic hydrogen production [23]. Recently, we have reported the combination of MoO_2 and graphene as highly efficient HER catalytic material [24]. In the current work, we report the HER catalytic activity of new MoP-graphite nanocomposite materials prepared by ball milling.

2. Experimental

Molybdenum phosphide (MoP, 99.5%) and graphite (crystalline, 300 mesh, 99%) were purchased from Alfa Aesar and used without further purification. Nanocrystalline molybdenum phosphide was prepared by ball milling the commercial MoP (referred to as C-MoP below) in a high-energy ball mill SPEX 8000M mixer/mill using tungsten carbide balls (10.74 g). MoP samples were milled for different periods of 0, 15, 30, 40, 60, 90, and 120 min to obtain samples labeled C-MoP, MoP-15, MoP-30, MoP-40, MoP-60, MoP-90, and MoP-120, respectively. In order to prevent compound overheating, a 15 min time delay was provided at 15 min intervals. We have termed the graphite after ball milling as graphite nanosheets, following the terminology employed previously for ball-milled graphite [20]. MoP-graphite nanosheets were prepared by mixing C-MoP and commercial graphite in different weight ratios in concentrated H_2SO_4 by stirring for nearly 1 h and then washing with water several times until the pH was neutral. The material obtained after vacuum filtration was dried in air at 60 °C overnight. The compounds obtained by mixing C-MoP and graphite in 1:1, 1:2, and 2:1 mass ratios are termed as MoP-G-11, MoP-G-12, and MoP-G-21, respectively. These compounds were then ball milled for 60 min and labeled as MoP-G-60-11, MoP-G-60-12, and MoP-G-60-21.

The MoP compounds were characterized with powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) surface area analysis. The powder XRD of the materials were acquired with PANalytical Empyrean X-ray diffractometer after spreading the powder samples over glass slides and scanning with a 0.013° step size. The crystallite sizes were estimated with Scherrer's approximation [25]. SEM images were collected by a Leo Zeiss 1530 VP scanning electron microscope operated at 10 kV. BET surface areas were obtained with a Quanta chrome instruments Nova 2200e Surface area and pore size analyzer.

For the HER activity studies, 1.5 mg of the catalyst was dispersed in 100 μL of Nafion (prepared by mixing 1 mL of 2 wt% Nafion solution and 9 mL of ethanol) by ultrasonication. Subsequently, 3 μL of the slurry was drop-casted on a clean glassy carbon electrode (GCE, 0.07 cm² area). The modified GCE was allowed to dry under ambient conditions. Each modified electrode was fabricated with identical loading. Electrochemical characterization was performed using a CH Instruments 660C electrochemical work station using a standard three-electrode setup. The electrocatalytic activity of the materials was evaluated using both linear sweep voltammetry (LSV) and cyclic voltammetry (CV). The electrochemical impedance spectroscopy measurements were carried out using a similar three electrode system. The impedance spectra were recorded under a perturbation signal of 0.5 V amplitude over a frequency range of 0.1 Hz–1 kHz. Gas chromatographic analysis of hydrogen evolved was carried out using Varian CP 3800 Gas chromatograph. The electrochemical cell was purged with nitrogen gas which also served as the carrier gas. The GC instrument was equipped with a thermal conductivity detector and a purge trap. For the GC experiments, another type of working electrode was prepared by coating 1 mg/cm² of material dispersed in Nafion solution over carbon fiber paper (Fuel Cell Stores) using a paint brush. All the measurements were carried out in 0.5 M H_2SO_4 solution.

3. Results and discussion

The powder X-ray diffraction pattern of C-MoP is shown in Fig. 1a. The stick pattern shows a perfect match with MoP with JCPDS No. 98-009-0157 (Fig. 1b). Molybdenum phosphide crystallizes in the hexagonal tungsten carbide (WC) structure in which each molybdenum atom is trigonal-prismatically surrounded by six phosphorus atoms, and vice versa (Fig. 1c). The MoP XRD pattern shows significant peak broadening and reduction in intensity with increased milling time. The diffraction peak broadening and intensity reduction in ball-milled powders are associated with the changes in crystallite size, lattice internal strain, and the instrumental effects [26].

We also characterized the mixed MoP-graphite materials before and after ball milling. We focus most of our analyses on the material prepared by mixing MoP and graphite in a 1:1 ratio (MoP-G-11). The XRD of MoP-G-11 (Fig. 2) before ball milling shows sharp peaks corresponding to C(002) crystalline reflections ($2\theta = 26°$) of graphite. After 60 min of ball milling (to correspond with the "optimum" MoP-60 in Fig. 1), the sharp C(002) peaks are significantly reduced in intensity with increased width. The peak width is a probe of structural disorder: narrow peaks are an indication that sp^2 clusters possess less defects and strain. Defect aggregation causes bond distortions at sp^2C=C sites, thus in-plane sp^2 bonds become strained and distorted and get converted to sp^3 bonds and consequently sp^2/sp^3 carbon ratio decreases with the increase in lattice defects. These lattice distortions disturb the conjugation of double in-plane bonds and also the spacing of the sp^2 carbon sites inducing microstructural and dimensional changes to the graphitic lattice. Thus the increase in width of the C(002) peak in