Synthesis And Characterizations Of Moo_x Supported On Carbon Black Electrocatalyst

Subhashini S, Vivek Thamizhmani, B.S.P.Shema

Abstract: Synthesis of MoO_x nanoparticles supported on carbon black as anode in proton-exchange membrane fuel cell has been carried out by two methods: (i) Conventional and direct impregnation method and (ii) Non-conventional and advanced strong electrostatic adsorption method. Formation of MoO_x nanoparticles supported on carbon black has been characterized by powder XRD. Effect of calcination temperatures on the formation of MoOx supported carbon has been investigated by powder XRD. Particulate properties such as BET specific surface area and particle size have been also investigated with different calcination temperatures.

Keywords: Adsorption, Electrocatalyst, Proton Exchange Membrane, Specific surface area, XRD

Introduction

Energy-related research has topical interest as evidenced from the 2019-chemistry Nobel Prize awarded to three innovative scientists (Akira Yoshino, M. Stanley Whittingham and John B. Goodenough) who have been working on lithium-ion battery materials (1-3).

Surge in energy-need demands active research on fuel cells (e.g. low temperature proton-exchange membrane fuel cell) to be practically viable for the next generation energy sources (4). Anode in the proton-exchange membrane (PEM) fuel cell involves oxidation process using noble metal(s) or noble metals alloy nanoparticles supported on carbon electrode The key issue of carbon monoxide (CO) poisoning associated with anode prevents practicability of PEM fuel cell (5). To some extent, the key issue of CO-poisoning can be fixed using noble metal alloy (e.g. Pt-Ru) nanoparticles supported on carbon. However, durability of the anode can't be survived at higher carbon monoxide concentration.Recent studies indicate the stability and durability of anode material can be increased using Pt and MoO_x nanomaterial's supported on carbon black for PEM fuel cells (6). Therefore, this article focuses on synthesis and characterizations of MoO_x supported on carbon black electrocatalyst as anode material for PEM fuel cells.

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2. Experimental:

(i) Synthesis of MoO_x nanoparticles supported on carbon black by conventional and direct impregnation method

This method involved direct impregnation of ammonium hepta molybdate on carbon black support. Thus, 10 wt.% Mo as ammonium hepta molybdate was synthesized using the steps given below:

1. 0.84g ammonium hepta molybdate was dissolved in 11.5mL water.
2. This clear solution containing 0.84g of ammonium hepta molybdate in 11.5mL water was added in every 50 microliter to 5g carbon black taken in a tube.
3. After the entire addition of aqueous solution of ammonium hepta molybdate to 5g carbon, the carbon black was kept at room temperature for 48hrs to dry.
4. It was then completely dried in air oven at 120degC for 17hrs.
5. Thermal decomposition of ammonium hepta molybdate on carbon black was explored to get MoO_x on carbon black.
6. The thermal decomposition was carried out either helium atmosphere or hydrogen atmosphere to minimize the loss of carbon black as CO_2.

(ii) Synthesis of MoO_x nanoparticles supported on carbon black by non-conventional and advanced strong electrostatic adsorption method

7.15 wt.% Mo as ammonium hepta molybdate on 2g carbon black was synthesized by strong electrostatic adsorption method using 50mL of 3000ppm ammonium hepta molybdate solution. 2g carbon black was put into 50mL of 3000ppm ammonium hepta molybdate solution with final pH of 2. This was allowed to shake for 1h in the shaker. Then, the solid was separated by filtration. The wet-solid was dried at room temperature for a couple of days. The thermal decomposition was carried out either helium atmosphere or hydrogen atmosphere to minimize the loss of carbon black as CO_2. Particle size was calculated from BET specific surface area using the equation as shown below:

Particle size (nm) = 6000/(BET SSA)*density

Where BET specific area was measured experimentally and density of carbon black was 0.154 g/cm^2. Particle size from

X-ray line broadening was calculated by Scherrer equation as shown below:

Particle size (nm) = Kλ/(B*cosθ)

Where K=constant, λ= wavelength of CuK_α in nm, B=line broadening in theta and cosθ = XRD peak position.

3. Results and discussion:

3.1. Synthesis of MoO_x supported on carbon by conventional direct impregnation method:

It is important to maximize the amount of MoO_x on carbon support by direct impregnation method. It is found based on pore volume of carbon that 2.3mL water is required for 1g carbon. Therefore, 10 wt.% Mo as ammonium hepta molybdate is synthesized by direct impregnation method using 0.83g ammonium hepta molybdate dissolved in 11.5mL water.

3.2. Synthesis of MoO_x supported on carbon by non-conventional strong electrostatic adsorption method:

In this method, it is essential to determine the optimum pH that is required for the maximum uptake of ammonium hepta molybdate on carbon. Thus, it is confirmed the optimum final pH of 1.88 for which 17.15wt.% Mo update by carbon.

3.3. Powder XRD characterization:

Powder XRD characterization is widely used to determine crystalline phase formation from the decomposition of precursor under controlled conditions. Fig.1 shows powder XRD patterns of MoO_x nanoparticles supported on carbon that is obtained at heating temperature of 500degC to decompose ammonium hepta molybdate that is loaded on carbon by conventional and direct impregnation method. It is evident from the Fig.1 that ammonium hepta molybdate supported on carbon calcined in helium atmosphere up to 400degC is X-ray amorphous and the formation of MoO_2 begins to form at 500degC. Therefore, it is possible to obtain MoO_2 by heating ammonium hepta molybdate supported on carbon at 500degC in helium for both samples of direct impregnation method and strong electrostatic adsorption method.

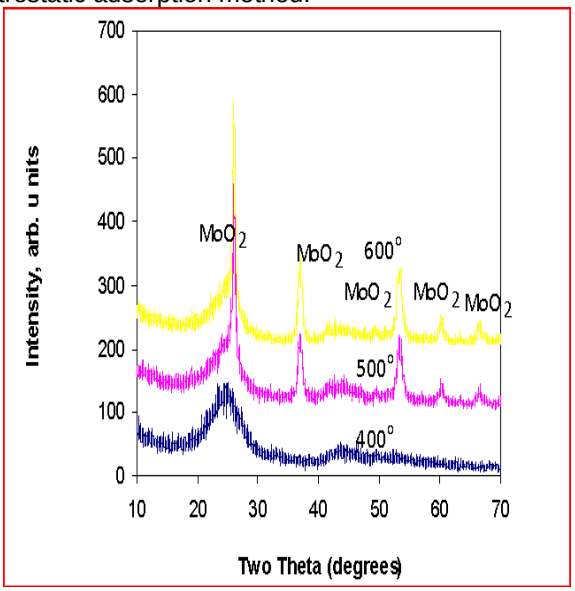

Fig.1: Powder XRD patterns with different calcination temperatures of MoO_x supported carbon

3.3. Particulate properties studies:

Particulate properties such as particle size and BET specific surface area are investigated in this study. Table 1 summarizes particulate properties (BET specific surface area, particle size from BET specific surface area and particle size from powder XRD line broadening) of MoO_x supported on carbon that is calcined at 300degC, 400degC, 500degC and 600degC. It is interesting to note that BET specific surface area increases with increase in calcination temperature (Fig.2).

Table 1: *Effect of calcination on particulate properties of MoO_x supported on carbon black in helium atmosphere for 1h (Direct impregnation method)*

Calcination Temperature, degC	BET specific surface area, m^2/g	Particle size (nm) from BET specific surface area	Particle size (nm) from XRD line broadening
300	123	7.54	X-ray amorphous
400	124	7.49	X-ray amorphous
500	189	4.91	28.22
600	200	4.64	28.22

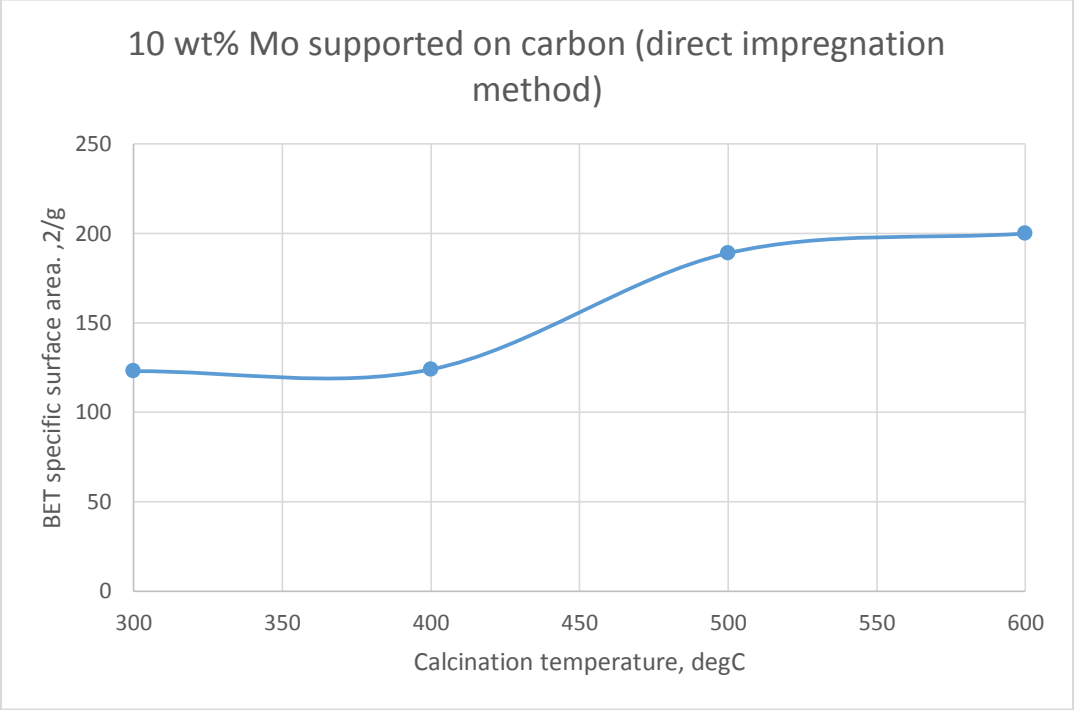

Fig.2: *Effect of calcination on specific surface area of 10wt.% MoO_x supported on carbon*

Particle size calculated for MoO_x supported on carbon from BET specific surface area is not true value since BET specific surface area does include carbon support in addition to MoO_x nano particles. Therefore, particle size calculated for MoO_x supported on carbon from XRD line broadening is explored. Thus, particle size of MoO_x on carbon that is calcined from XRD line broadening at 500degC and 600degC remains the same. It indicates that during calcination of MoO_x supported on carbon at 500degC and 600degC for 1h there is no growth of MoO_x that is supported on carbon.

4. Summary and Conclusions:

1. Controlled synthesis of MoO_x supported on carbon has been achieved by two methods; Conventional direct impregnation method and non-conventional strong electrostatic adsorption method.
2. Powder XRD characterization confirms the formation of MoO_2 nanoparticles at above 500degC.
3. XRD line broadening reveals that there is no growth of MoO_2 nanoparticles up to 600degC annealing temperature.
4. These methods can be extended to synthesize other metal oxide(s) and/or metal nanoparticles supported on carbon or porous materials.

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