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Cubic Mn_2O_3 nanoparticles on carbon as bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions

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ABSTRACT

Transition metal oxides are most promising non-platinum catalysts for oxygen reduction (ORR) and oxygen evolution reactions (OER) in renewable-energy technologies. Among transition metal oxides, Mn oxides are very active for both ORR and OER and can act as a bifunctional catalyst. But due to their poor electronic conductivity, carbon materials are used as supports or mixed with other metal oxides to increase their conductivity that assistances in electrochemical applications. Herein, a highly active mesoporous cubic material consisting of Mn_2O_3 nanoparticles grown on carbon (Vulcan XC-72 R) as a high performance bifunctional catalyst for both ORR and OER have been synthesized. The synthesized Mn_2O_3/C has been characterized by various structural analyses. The Mn_2O_3/C material exhibits much better ORR activity compared to the commercially available Pt/C and Pd/C in alkaline media. The same material is also active for OER, making it a bifunctional electrocatalyst for both the reactions. Consequently, Mn_2O_3/C is quite stable up to 1000 cycles displaying its better stability. The reaction mechanism follows a 4-electron pathway for ORR. The superior electrocatalytic presentation mainly arises due to the better synergistic coupling effect of carbon and Mn_2O_3.

1. Introduction

The world's ever-growing energy demand combined with the crisis of natural resources inspired the researchers towards extensive exploration of sustainable and renewable energy sources [1]. To overcome these shortcomings, alternative energy storage and conversion devices such as, metal air batteries, fuel cells and water splitting systems have been widely employed as efficient and clean energy sources [2]. Fuel cells are considered to be superior energy converters capable of converting chemical energy of fuels (e.g. hydrogen, methanol, ethanol, etc.) into electrical energy [3]. Among different types of the existing fuel cells, proton exchange membrane fuel cells (PEMFCs) have attracted enormous attention owing to its advantages such as low operation temperature, high energy density, high energy conversion efficiency and more eco-friendly and find wide application in transportation, portables and stationary devices [4]. Similarly, a metal-air battery, characterized by an open cell structure also produces and stores energy via a redox reaction between metal and oxygen in air [5]. However, for worldwide commercialization of these applications in terms of cost, efficiency and longevity, high performance oxygen electrodes are needed [6]. One of the most important reactions that take place in the cathode of fuels cells as well as metal air batteries is the oxygen reduction reaction (ORR) [7,8]. Moreover, oxygen evolution reaction (OER) that generates oxygen during water oxidation is also of great interest due to its significance in the energy conversion devices [9,10]. Both the reactions i.e. ORR and OER depends extremely on the catalyst as well as the electrolyte used and proceed via a four electron reaction pathway involving various intermediates and suitable mechanisms [11]. One of the key drawbacks of both the fuel cells and the metal-air batteries, which lead to loss of cell efficiency, is the sluggish kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) that takes place at the cathode and anode of these electrochemical devices [12]. Thus, developing desirable nanocatalysts to overcome the sluggish kinetics of ORR and OER is one of the most demanding tasks [13]. In general, state-of-the-art platinum/carbon (Pt/C) catalyst or platinum based materials are considered to be the best catalyst for ORR and OER in both alkaline and acidic medium due to its excellent electrocatalytic activity [14–16]. However, the high cost, scarcity and low durability prevent its extensive commercial applications. Therefore, much effort has been given towards exploration of cost effective, durable and highly abundant alternative electrocatalysts

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with comparable or even higher catalytic performance than that of platinum-based electrocatalysts [17–19].

Replacing platinum with inexpensive metals, developing metal free electrocatalysts or transition metal oxide – based electrocatalysts are ideal approaches to reduce the cost of the electrocatalysts [20,21]. Transition metal oxide (Metal = Ir, Mn, Fe, Co etc) based electrocatalysts have been emerged as an inexpensive alternatives to precious Pt-based materials with outstanding ORR performance [22,23]. Experimental and theoretical reports have shown that transition metal oxides based electrocatalysts act as very suitable electrode material in various electrochemical devices [24]. Recently, manganese oxides (MnO_x) have drawn enormous attention as an appealing ORR catalyst in alkaline medium owing to its high stability, availability, low cost, variable oxidation states and effective catalytic properties [25,26]. Such catalysts with versatile crystallographic structures include MnO, MnO_2, Mn_2O_3, Mn_3O_4 has the potential to replace the expensive benchmarked Pt/C catalysts [27]. The catalytic activity of these oxides is morphology and stoichiometry dependent [28].

Metal catalysts sometimes undergo agglomeration, dissolution and sintering during fuel cell reactions which results in diminishing catalytic activity and stability [29]. Hence, for proper dispersion and to prevent agglomeration the use of an ideal support is very essential [30]. Carbon-based materials have been widely used as catalyst supports in many reactions such as chemical and enzymatic biomass transformation reactions, fuel cell reactions, metal air batteries etc. due to its high specific surface areas, high chemical resistivity, high porosity, superior mechanical strength, excellent electron conductivity and relative chemical inertness [31,32]. The reason behind wide use of carbon-based materials as catalyst supports is the ease of its fabrication in different physical forms and shape. In case of precious metals (like Pt and Pd), the use of graphene and carbon nanotubes (CNTs) as supports is more as compared to other carbon-based supports to improve ORR activity and stability [33,34]. Carbon based materials not only act as active supports but also enhances the poor electronic activity of the transition metal oxide – based electrocatalysts [35]. Thus, the combination of transition metals with carbon support turned out to be promising electrocatalysts that could remarkably increases the catalytic activity and durability owing to their synergistic effects [36].

Herein, we have obtained cubic-Mn_2O_3 nanomaterials supported on Vulcan XC-72 R carbon electrocatalyst via hydrothermal method at 120 °C to investigate its bifunctional electrocatalytic activity towards ORR and OER. The synthesized nanoparticle was found to show high electrocatalytic activities, enhanced mass activity and superior stability in alkaline media as compared to the commercially available Pt/C and Pd/C catalyst. Thus the present work highlights an improved strategy for enhancing the catalytic activity of Mn-oxide nanoparticles toward ORR and OER.

2. Experimental section

2.1. Materials

The chemicals used in this work were manganese chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$), urea and Vulcan XC-72 R carbon black. All the chemicals used were of analytical reagent grade and used as received without further purification. Urea and $MnCl_2{\cdot}H_2O$ were purchased from MERCK specialties Pvt. Ltd. (Mumbai, India). Vulcan XC-72 R carbon black was obtained from Cabot Corporation.

2.2. Synthesis of Mn_2O_3/C nanoparticles

Typically, 0.647 g of $MnCl_2{\cdot}4H_2O$ was dissolved in 40 mL of distilled water. Subsequently, 40 mL of 2.40 g urea was added drop wise to the freshly prepared solution from a burette and stirred for 30 min. The resulting solution is transferred to a 150 mL teflon-lined stainless steel autoclave which was then kept in an oven maintained at a temperature of 120 °C for 6 h. Finally, it was allowed to cool for 15 h then washed, centrifuged with distilled water and with absolute alcohol and dried at 50 °C. The precursor was then calcined in a muffle furnace at 450 °C for 4 h. Again Mn_2O_3/C was prepared by mixing 0.060 g Mn_2O_3 with Vulcan XC-72 R carbon powder in 20% weight ratio, ground for 30 min in an agate mortar and the mixture was ultrasonicated with ethanol (as a solvent) for 30 min. The mixture was allowed to first air dry and then kept in an oven at a temperature of 50 °C.

2.3. Characterization

TGA curve was obtained on a thermal analyser (Model TGA-50, Shimadzu) instrument. The samples were heated from ambient temperature to 600 °C under N_2 flow at heating rate of 10 °C min^{-1}. X-ray diffraction was used to investigate the bulk phases present in the samples. The powder X-ray diffraction patterns were recorded on D8 FOCUS (BRUKER AXS, GERMANY) instrument. The intensity data were collected over 2θ range of 10–80°. Infra-red spectra were measured in a FTIR spectrophotometer, Model Nicolet Impact I-410. Measurements were performed by pelletizing the samples with KBr in the mid-IR region. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. To study the surface topography, SEM analysis were carried out with JEOL, JSM model 6390 LV scanning electron microscopes, operating at an accelerating voltage of 15 kV. The TEM investigations were carried out on TECNAI G^2 20 S-TWIN (FEI COMPANY, USA) having resolution of 2.4 Å equipped with a slow scan CCD camera and an accelerating voltage of 200 kV. Raman spectroscopy has been extensively employed to discriminate between different structures on oxide surfaces. Raman spectra were collected using 514 nm laser source in a RENISHAW, UK Raman spectrometer under ambient conditions. BET surface area was determined by N_2 adsorption-desorption using a Quantachrome instrument (Model: NOVA 1000e). The pore size and pore volume were determined following Barrett-Joyner-Halenda (BJH) method in the same instrument. The XPS studies were performed using a Thermo K-Alpha XPS equipped with an Al Kα radiation (1486.6 eV) X-ray source at a pressure < 10^{-7} Torr and an electron take-off angle (angle between electron emission direction and surface plane) of 90°. A survey scan was performed using pass energy of 200 eV to determine possible contaminants. The binding energies of the samples were charge-corrected with respect to the adventitious carbon (C 1s) peak at 284.6 eV.

2.4. Fabrication of electrodes and electrochemical measurements

All the measurements were performed under identical conditions. The working electrode was prepared by dispersing 5 mg of Mn_2O_3/C in 0.5 mL of ethanol-water and 0.5 mL nafion solution (0.5 wt.%). To get a homogeneous suspension the mixture was ultrasonicated for 30 min. Then 6 μL was loaded on the surface of the glassy carbon electrode with a diameter of 3 mm and dried slowly in N_2 atmosphere at 35°C in a vacuum oven to achieve a uniform surface. Finally a Pt/C and Pd/C catlalysts were used as comparison and fabricated exactly as the Mn_2O_3/C. Electrochemical measurements were performed in 0.1 M KOH electrolyte in a standard three electrode cell at room temperature using an Autolab PGSTAT 204 potentiostat/galvanostat (Metrohm, Autolab,

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