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Manganese oxide with different morphology as efficient electrocatalyst for oxygen evolution reaction

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ABSTRACT

Three-dimensional (3D) manganese oxides consisted of tetragonal phase Mn_3O_4 and α-MnO_2 with different morphology have been directly grown vertically on Ti foil by a simple electrochemical method without any template and used as the catalysts for oxygen evolution reaction (OER). The results show that manganese oxides with different morphology show high activity and good stability for OER and the manganese oxide (MnO_x) nanowire arrays obtained at 70 °C show higher activity and better stability than MnO_x with cotton wool structure and MnO_x nanosheet arrays.

Introduction

As the fossil energy continuously running out, the demand for sustainable and renewable energy sources such as wind, tidal, geothermal and solar energy systems which are used as power generation systems is in constant growth [1]. However, the power output of these energy systems is dependent on climatic and geographic conditions [2]. Hydrogen energy which can be used as a fuel to get a reliable power for almost every application that fossil fuels are used is regarded as one of the most promising energy carriers in the future and it can be used for methanation of CO_2, combustion processes, and conversion back into electricity by fuel cells [3]. Among different possible methods, the electrochemical gas evolution during water electrolysis has attracted more and more attention as one of sustainable and renewable chemical technologies for producing hydrogen [4]. There are two half-reactions of electrochemical water electrolysis in alkaline media: the anodic oxygen evolution reaction (OER, $4OH^- = 2H_2O + 4e + O_2$) and the cathodic hydrogen evolution reaction (HER, $2H_2O + 2e = 2OH^- + H_2$). In these two half-

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reactions, the OER requires to form two oxygen–oxygen bonds in the four-electron redox processes by transfer proton and electron, which results in more kinetically demanding for the OER [5,6]. To address this problem, considerable efforts have been devoted to explore the electrocatalysts with low OER overpotential [7–9]. Currently, the most active catalysts are the rutile type oxides RuO_2 and IrO_2 which show the lowest OER overpotential, however theses oxides are limited their application in industrial processes, owing to their poor chemical stability in alkaline media and the high price and limited supply of Ru and Ir [10–13]. Furthermore, recent reports have shown that some transition metal oxides such as Cu oxide [14,15], cobalt oxide [16–19], nickel oxide [20–22] are being widely explored for OER electrodes because of their low cost, low toxicity, and great flexibility in terms of structure and morphology. Manganese oxides have shown an activity for the OER and manganese is earth-abundant element [23–27].

Recently, three-dimensional (3D) nanostructure arrays have been used for electrochemical system because of their unique structural and electronic properties [28–33]. Unlike the bulk materials, the 3D arrays such as nanowire/nanosheet arrays are the most attractive materials due to their high interfacial area between electrode and electrolyte for charge transport and fast electrical pathways among the numerous nanostructures [34–40]. According to the recent research, such structure permits reactants to diffuse into the catalyst layer easily and form a larger three-phase interface, resulting in the reduction of liquid sealing effect, hence improve the catalyst performance [41]. Lei and his cooperators have reported that Ni–Co–O@Ni–Co–S hierarchical nanowire arrays show significantly improved activity for OER [42]. Wang and his cooperators have reported that hierarchically Ni_3S_2 nanorod arrays exhibit low overpotential of 200 and 217 mV at current density of 10 mA cm^{-2} for HER and OER [43]. The hierarchical nanowire arrays can offer a higher surface area and porosity, while the conductivity can be well preserved. The hierarchical porosity could accelerate the diffusion of the OH^- ions, thus resulting in faster kinetics [44]. Coating this architecture onto metal substrates can improve the conductivity of electroactive materials and shorten the electron and ion-diffusion pathways, with the aim of more efficient charge and mass exchange [45]. Cheng and his cooperators have reported that nickel oxide nanosheet arrays on carbon cloth and $Cu(OH)_2$–CuO nanorod arrays show high catalytic activity with an onset potential (E_{onset}) of 295 and 350 mV for OER [14,46]. Jiang and his cooperators have reported that nickel cobalt layered double hydroxide nanosheet arrays on nickel foam show excellent OER activity in alkaline medium with an onset overpotential as low as 290 mV, large anodic current density and excellent durability [47].

In this paper, manganese oxides with different morphology are directly grown on Ti foil with different temperature by a simple electrochemical method. Ahmed and his cooperators have synthesized nanocrystalline copper nanoparticles with varied morphology, nanocubes, nanorods and nanospheres as catalysts for HER and OER. Cube-shaped nanoparticles show significantly high hydrogen and oxygen evolution efficiencies compared to the nanorods and spherical nanoparticles [48]. Ahn and his cooperators have investigated the release of active sites blocked by bubbles attached on the surface of nickel catalysts with four different morphologies of a nickel catalyst during the OER in alkaline water electrolysis and concluded that Ni catalysts with hierarchical morphology are beneficial for the electrolysis of water due to their high catalytic activity (large surface roughness) and the ability to detach bubbles from their surface (high wetting ability) [49]. Here, the effect of different morphology of manganese oxides on OER will be compared. At the reaction temperature of 40 °C, MnO_x cotton wool structure was obtained. At the reaction temperature of 70 °C and 90 °C, the morphology and microstructure of MnO_x obtained were nanowire arrays and nanosheet arrays, respectively. Through the performance of the characterization, it will be seen that manganese oxides with different morphology have different activity and stability for OER.

Experimental

The manganese oxides with different morphology were electrodeposited on the Ti (1 cm × 2 cm × 0.2 mm, 99.99%) substrate in a solution of 0.01 mol L^{-1} $MnAc_2$ + 0.02 mol L^{-1} NH_4Ac + 10% dimethyl sulfoxide (DMSO) with a current density of 0.75 mA cm^{-2} for 20 min at different temperature. All reagents used were of analytical grade purity and purchased from Sigma Aldrich. The Ti foil was cleaned ultrasonically in distilled water, hydrochloric acid, ethanol, acetone and then rinsed in distilled water again and dried before being used. The deposition was carried in a conventional three-electrode glass cell via an electrochemical approach without any template. The Ti foil and a graphite rod were used as working electrode and counter electrode, respectively. The saturated calomel electrode (SCE, 0.241v. versus RHE) was used as reference electrode, which was connected to the cell with a double salt bridge. The electrochemical OER of prepared products was carried out in a three-electrode cell using CHI700C electrochemical workstation (Chenhua, Shanghai) in room temperature. The three-electrode cell was consisted of the product prepared on Ti foil substrate as working electrode, SCE as reference electrode and the platinum foil (3.0 cm^2) as counter electrode.

X-ray diffraction (XRD) was carried out using a Panalytical X'Pert powder X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm). Scanning electron microscopy (SEM) images were obtained using a Quanta 400 FEG microscope (FEI Company). Transmission electron microscopy (TEM) images were carried out on a JEOL JEM-2010 (JEOL Ltd.).

Results and discussion

It's known that the deposition temperature is one of most important parameters for formation MnO_x with different microstructure and morphology [50]. Fig. 1 shows the SEM images of manganese oxides with different morphology grown on the Ti substrate in different temperature. Fig. 1a and b shows the SEM images of MnO_x synthesized at 40 °C with a 3D loose networks of cotton wool structure. When the