



Influence of synthesis parameters on amorphous manganese dioxide catalyst electrocatalytic performance



Adeline Loh^a, Ke Xu^b, Xiaohong Li^{a,*}, Baoguo Wang^{b,*}

^a Renewable Energy Group, College of Engineering, Mathematics and Physical Sciences, University of Exeter, Penryn Campus, Cornwall TR10 9FE, UK

^b Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 23 February 2017

Received in revised form 16 May 2017

Accepted 28 May 2017

Available online 1 June 2017

Keywords:

amorphous manganese dioxide
oxygen reduction reaction
gas diffusion electrode
alkaline electrolyte

ABSTRACT

Oxygen reduction reaction (ORR) catalysts with applications in fuel cells and metal-air batteries can be tailored to overcome the slow kinetics and to reduce overpotentials of the reaction. In this work, a series of amorphous manganese dioxides are synthesised via a chemical redox synthesis method. Synthesis parameters including molar ratio, the order of adding sequence of reactants, pH, and temperature are found to affect the catalyst's physical and chemical properties such as morphology, lattice hydration, active surface area, and surface properties. The samples are characterised by SEM, BET, XPS and XRD as well as cyclic voltammetry, rotating disc electrode, and gas diffusion electrode measurements. The results indicated that an optimal catalyst sample can be synthesized by reduction of KMnO_4 with $\text{Mn}(\text{CH}_3\text{COO})_2$ in $\text{MnO}_4^-/\text{Mn}^{2+}$ molar ratio of 2.67 by addition of KMnO_4 into $\text{Mn}(\text{CH}_3\text{COO})_2$ at pH 12, 295 K. The gas diffusion electrode coated with amorphous manganese dioxide catalyst ink in 10:10:2 wt% of $\text{MnO}_2:\text{XC-72R}:\text{PTFE}$ with a loading of 2 mg cm^{-2} , was shown to support current densities up to 100 mA cm^{-2} with improved performance.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Oxygen electrodes are found in energy conversion and storage applications such as hydrogen production in water electrolyzers, transportation and power generation by fuel cells, and large-scale energy storage by metal-air secondary batteries. These applications require improved performance of oxygen electrodes in the form of durability, lifetime, efficiency, and cost, in order to attain widespread commercialisation. The rate of the oxygen reduction reaction (ORR) is unfortunately very sluggish; electrocatalysts are thus essential to provide lower activation energy pathways to speed up ORR rates to a desirable level. Precious metals and their alloys are considered the most effective ORR catalysts [1–3] due to their inert quality in aqueous electrolytes, however, they are far too expensive for practical application. Extensive research effort [4] has been made to explore non-precious metals and their oxides, such as MnO_2 , Co_3O_4 , and perovskite oxides etc., as electrocatalyst materials to obtain effective low cost oxygen electrodes.

Of these, MnO_2 is highly appealing because (i) manganese is cheap and abundant in the earth compared to precious metals [5,6]

that leads to cost-competitiveness and hence more suitable for large-scale commercialisation, (ii) manganese and its oxides are low in toxicity and environmentally-friendly, and (iii) manganese has three oxidation states of +2, +3 and +4 near the equilibrium potential of the ORR reaction [7] with a variety of polymorphic forms (e.g. α -, β -, γ -, δ -, ϵ -) and morphologies of micro- and mesoporous manganese oxides, all of which make it suited for modification to give better electrochemical performance. Research has shown that a diversity of properties of manganese oxides depends on the specific synthetic route. These differences can be attributed to variations in particle size and the type and amount of defects in the structures. For this reason, small changes in synthetic parameters can result in materials with novel catalytic, electrochemical, and ion-exchange properties [8]. For example, Luo and Suib [9] carried out a study on the effect of altering parameters such as molar ratio of $\text{MnO}_4^-/\text{Mn}^{2+}$, basicity, addition of magnesium and temperature of the aging process on the crystallisation of birnessites. They found that fast crystallisation rates were achieved at higher aging temperatures, higher basicities and molar ratios between 0.28 and 0.36. Kanungo and Mahapatra [10] reported that preparing hydrous MnO_2 at mild alkaline conditions of pH 8.0 to 8.5 would result in a higher percentage of H_2O content in the structure. A more recent study [11] on amorphous birnessites reported that the rate of mixing and

* Corresponding authors.

E-mail addresses: X.Li@exeter.ac.uk (X. Li), bgwang@tshinghua.edu.cn (B. Wang)

addition sequence of synthesis reactants as well as varying pH change the morphology and textural properties of the products.

In this work, a number of amorphous MnO_2 samples have been synthesized with a simple chemical preparation method. Synthesis parameters such as molar ratio of $\text{MnO}_4^-/\text{Mn}^{2+}$, addition sequence of reactants, pH, and temperature are varied in the synthesis procedure to produce a range of catalysts which are then tested for ORR performance with rotating disc electrode (RDE) apparatus as well as a custom-built gas diffusion electrode (GDE) cell. Spectroscopic and electrochemical methods were employed to evaluate the relationship between the synthesis parameters and surface morphology and properties of the amorphous MnO_2 -based electrodes.

2. Experimental

2.1. Synthesis of amorphous MnO_2 catalysts

The catalyst was prepared by a chemical redox method which was chosen because the preparative parameters such as temperature and basicity of the mixture, precursor and solution concentration can be controlled for better catalyst morphology. In a typical synthesis procedure, 50 mL, 0.04 M KMnO_4 (Fisher Scientific, 99%) was added to 100 mL, 0.03 M $\text{Mn}(\text{CH}_3\text{COO})_2$ (Fisher Scientific, 98%) with constant stirring. A precipitate formed upon the addition of one reactant to the other. The pH of the resulting mixture was measured to be approximately pH 5 and then adjusted to a basic value using 4 M sodium hydroxide (Fisher Scientific, 98%) according to previous preparation procedure [12]. The precipitate was collected by centrifuging the mixture 3–5 times at 2500 rpm for 20 minutes at a time. The deposit was washed with deionised H_2O until the purple colour of permanganate ions was no longer seen, and then collected, dried overnight at 333 K and ground down to a fine powder. The altered conditions include $\text{MnO}_4^-/\text{Mn}^{2+}$ molar ratio, synthesis pH, temperature, and the order of addition sequence which the reactants were added to each other such as adding KMnO_4 to $\text{Mn}(\text{CH}_3\text{COO})_2$ (denoted as A) and vice versa (denoted as B). Table 1 provides the details of the catalysts synthesised under various conditions. The annealed catalyst sample was treated at 873 K in air for 3 h and left to cool overnight.

2.2. Preparation of RDE samples

The catalytic activity of the MnO_2 samples was characterised by rotating disc electrode (RDE) voltammetric measurements, carried out in alkaline electrolyte of 1 M NaOH. A well-dispersed catalyst ink was prepared by mixing 1 mg of electrocatalyst with 1 mL deionised H_2O , 0.5 mL isopropanol and 5 μL of 5 wt% Nafion 117, used as received (Sigma-Aldrich). The ink was ultrasonicated for a minimum of ~ 30 mins, then homogenised at 28 000 rpm for 3–4

mins using a Cole-Parmer LabGEN 7 series homogeniser. The catalyst ink was loaded onto a glassy carbon working electrode (Pine Instrument Company) of 4 mm in diameter (working area = $\sim 0.126 \text{ cm}^2$) to measure electrochemical performance of the catalyst. Aliquots of the catalyst ink were loaded onto the glassy carbon surface using a micropipette, with drying in between each aliquot to give a final loading of $\sim 120 \mu\text{g cm}^{-2}$.

2.3. Preparation of GDE samples

Catalyst inks were prepared by mixing together the synthesized MnO_2 , carbon powder (Vulcan XC-72R, Cabot Corp., 100%) and polytetrafluoroethylene (PTFE) solution (Aldrich, 60% dispersion in H_2O by weight). A solvent of isopropanol and deionised water in a 1:1 weight ratio was firstly added into the PTFE solution to give a homogenous mixture. This PTFE solvent mixture was then poured into the catalyst and carbon powder to make the catalyst ink. The ink was sonicated for ~ 15 mins before being homogenised at 28 000 rpm for ~ 4 mins to ensure the ink was homogenous.

Several thin layers of catalyst ink mixture were spread onto the pre-cut carbon paper (Alfa Aesar, base-layered carbon paper) with an area of 1.3 cm^2 using a stainless steel spatula until the desired loading was reached. The performance of the GDEs was further improved by optimising the ratio of catalyst to carbon powder, ratio of catalyst to PTFE binder, and the catalyst loading.

2.4. Sample characterisation

2.4.1. Structural and morphological characterisation

The surface morphology of the samples was characterised using a Hitachi S-3200N scanning electron microscope (SEM), operated at an accelerating voltage of 20 kV and a working distance of 15 mm. Powder X-ray diffraction (XRD) results were collected on a Bruker D8 Advance X-ray Diffractometer with Cu tube source ($\lambda = 1.5418 \text{ \AA}$) and analysed using Bruker Diffraction Suite EVA software. Surface area was determined by N_2 gas sorption (Quantachrome Autosorb-iQ gas sorptometer) via the conventional volumetric technique. The sample was evacuated for 3 h at 473 K under vacuum prior to the measurement of surface area. The textural properties were determined via N_2 sorption at 77 K. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method based on adsorption data in the partial pressure (P/P_0) range of 0.02–0.22. The chemical states of Mn and O in the samples were determined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, ESCALAB 250Xi, Source: Al $\text{K}\alpha$) and analysed with XPS peak software (version 4.1).

2.4.2. Electrochemical measurements

All electrochemical measurements were carried out using Biologic potentiostat instrumentation with EC-Lab software. To obtain cyclic voltammograms, the potential was reversibly scanned at a scan rate of 50 mV s^{-1} . For ORR polarization curves, the potential was swept from 0.1 to -0.5 V at a scan rate of 5 mV s^{-1} . The current density is reported as a function of the electrode's geometric surface area. A Pt mesh and Hg/HgO in 1 M NaOH electrode were used as the counter and reference electrodes respectively. The working glassy carbon RDE tip was polished with MicroCloth (Buehler) and alumina powders, $1.0 \mu\text{m}$ and $0.5 \mu\text{m}$ (MicroPolish, Buehler) consecutively and cleaned ultrasonically in deionised H_2O before use. Fresh electrolyte was used for each run, the cell temperature was equilibrated to 298 K and electrolyte was saturated with gaseous oxygen or nitrogen with a glass frit of porosity 25–50 μm for minimum 30 mins prior to measuring voltammograms.

Electrochemical measurements of GDE samples were carried out in a standard three electrode set-up [13] consisting of a glass

Table 1
 MnO_2 samples synthesised at various parameters.

Sample Name	$\text{MnO}_4^-/\text{Mn}^{2+}$	pH	Temperature (K)
A1	0.33	12	295
A2	0.67	12	295
A3	0.67	12	333
A4	1.33	12	295
A5	2.67	12	295
A6	2.67	10	295
A7	2.67	8	295
A8	5.33	12	295
A9	0.67	5	295
B4	1.33	12	295
B5	2.67	12	295

A and B refer to the order of adding reactants. A: KMnO_4 added into $\text{Mn}(\text{CH}_3\text{COO})_2$ and vice versa for B.

Download English Version:

<https://daneshyari.com/en/article/6470825>

Download Persian Version:

<https://daneshyari.com/article/6470825>

[Daneshyari.com](https://daneshyari.com)