Journal of Power Sources 267 (2014) 33–38

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Microspheres assembled by KMn_8O_{16} nanorods and their catalytic oxygen reduction activity in direct methanol fuel cells

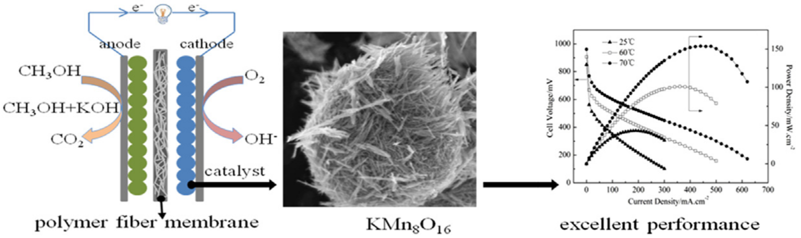
Yuan Fang, Xiaodong Yang, Li Wang, Yongning Liu*

State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, PR China

HIGHLIGHTS

- KMn_8O_{16} microspheres are assembled by nanorods with length of 300–1000 nm.
- The KMn_8O_{16} shows excellent tolerance toward methanol poisoning and good stability.
- The electron transfer number was measured to be about 3.98 by RRDE.
- The cost of our novel alkaline DMFC is half of conventional DMFCs.
- The performance approaches the highest value of DMFCs with noble catalysts.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 January 2014
Received in revised form
16 April 2014
Accepted 17 April 2014
Available online 4 May 2014

Keywords:
KMn_8O_{16}
Oxygen reduction reaction
Methanol tolerance
Direct methanol fuel cell

ABSTRACT

Microspheres assembled using cryptomelane-type KMn_8O_{16} nanorods are synthesized via a facile template-free, single-step hydrothermal technique. The synthesized KMn_8O_{16} generates nanorods 10–20 nm in diameter and approximately 300–1000 nm long. The rods self-assemble to form microspheres of 2–6 μm in diameters. The electron transfer number for KMn_8O_{16} during the ORR is approximately 3.98 at 0.5 V vs. Hg/HgO, and the H_2O_2 percentage is 0.66%. Moreover, a direct methanol fuel cell (DMFC) is built using KMn_8O_{16} as cathodic catalyst, PtRu/C alloy as the anodic catalyst and a polymer fiber membrane (PFM) instead of a conventional polymer electrolyte membrane (PEM). The peak power densities (43.3 mW cm^{-2} and 153.9 mW cm^{-2}) have been achieved at 25 °C and 70 °C, respectively. KMn_8O_{16} shows good electrocatalytic activity and stability during oxygen reduction in alkaline solutions and demonstrates tolerance toward methanol poisoning.

1. Introduction

Fuel cells convert chemical energy directly into electrical energy, making them promising energy-generating devices in industry, housing and traffic. Among them, direct methanol fuel cells (DMFCs) are gaining considerable interest due to their high energy density (6100 Wh kg^{-1} at 25 °C), low-to-zero emission and relatively low operating temperature [1–4]. Moreover, methanol is easy to deliver and store, quick to refuel and low cost [5]. However, several challenges, including the sluggish oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) kinetics, as well as the high cost of the Pt catalyst and polymer electrolyte membrane (PEM), impede the commercialization of DMFCs [3,6,7].

Recently, a type of polymer fiber membrane (PFM) has demonstrated improved performance at a reduced cost in liquid fuel cells; this material is an excellent alternative to PEM in DMFCs and DBFCs [8,9]. PFM are liquid-permeable membranes. The fibers in these membranes are neutral, in which the pores and gaps allow

---

* Corresponding author. Tel.: +86 29 8266 4602; fax: +86 29 8266 3453.
E-mail address: ynliu@mail.xjtu.edu.cn (Y. Liu).

http://dx.doi.org/10.1016/j.jpowsour.2014.04.085
0378-7753/© 2014 Elsevier B.V. All rights reserved.

liquid fuel and ions to transport or move through the PFM freely. If methanol passes through the membrane from the anode to the cathode, it should be converted into carbon dioxide by cathodic catalysts, such as Pt or Pt-based alloys, creating a mixed potential at the cathode [2,10–13]. Therefore, the cathodic catalysts must have excellent tolerance toward methanol poisoning in addition to good stability.

To overcome this issue and achieve an acceptable power output, we are developing a methanol-tolerant and non-noble oxygen reduction catalyst. Many studies have focused on Pt-free catalysts, such as Pd–Co [14], Pd–Fe [15], Ir–Se chalcogenide [16], RuSe/CNT [17], ordered mesoporous carbon nitride [18], Fe–CA–N [19] and Co–CA–N [19]; these catalysts have ORR catalytical activity and can tolerate methanol.

In recent years, manganese-based oxides (MnO_2, $Li_xMn_2O_4$, etc.) have received increasing attention due to their abundance, non-toxicity and environmental friendliness during many technological applications [20–23]. The ORR activities of MnO_2 in alkaline media have been researched, and its catalytic activity strongly depends on the crystal structures [24]. Among the various forms of manganese-based oxides, we are interested in cryptomelane-type KMn_8O_{16}; this mixed-valent compound primarily contains Mn^{4+} with a small fraction of Mn^{3+} [25]. Structurally, the cryptomelane-type KMn_8O_{16} materials have an octahedral molecular sieve (OMS) structure built from double chains of edge-sharing MnO_6 octahedra, forming $(2 \times 2) + (1 \times 1)$ tunnel structures with K^+ situated in the large (2×2) tunnels [26].

Several reports have detailed preparative methods for cryptomelane-type OMS, such as microwave heating, reflux and hydrothermal treatment, possibly generating different morphologies, particle sizes and particle distributions [27–31]. Cryptomelane-type KMn_8O_{16} shows promising utility as an electrode material for rechargeable lithium batteries [28,31], and a catalyst for oxidizing harmful organic substances, such as formaldehyde [29], styrene [32] and olefins [33].

In this work, we report the ORR activity and methanol tolerance of KMn_8O_{16} in a new DMFC system. In this DMFC system, we used KMn_8O_{16} to catalyze ORR, PtRu/C as an anodic catalyst and PFM as a replacement for PEM; this system delivered a promising performance and good stability compared to the literature data. The KMn_8O_{16} nanorods were prepared using a facile, template-free and single-step hydrothermal process. The crystal structure, morphology and electrochemical properties of the nanorods were studied.

2. Experimental

2.1. Catalyst preparation and characterization

All reagents were analytical grade. Cryptomelane-type KMn_8O_{16} were prepared using a template-free, single-step hydrothermal process. $MnSO_4 \cdot H_2O$ (1.7 g) and $KMnO_4$ (2 g) were each dissolved in 40 mL of distilled water containing 1 mL of concentrated HNO_3 to provide an aqueous reaction medium. The solution was stirred vigorously at room temperature for 30 min, immediately forming a dark brown precipitation. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 80, 100 and 120 °C for 24 h without shaking or stirring. After the mixture was cooled to room temperature, the brown precipitate was washed with distilled water several times and dried overnight at 80 °C. The three representative samples were designated KMO-80, KMO-100 and KMO-120 and were synthesized at 80, 100 and 120 °C, respectively.

The PtRu/C (HiSpec 10000) was purchased from Johnson Matthey (UK). The PFM (thickness = 159.3 μm) was purchased from the Nippon Kodoshi Corporation. The structure and physical properties of the PFM are described in the supplementary information of our previous work [9]. The samples of MnO_2 and Pt/C (HiSpec 3000) used for comparison were purchased from J&K Chemical Ltd. and Johnson Matthey (UK), respectively.

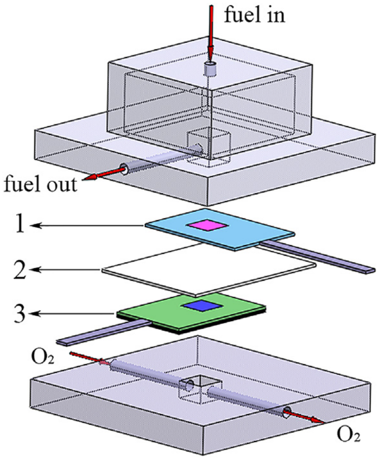


Fig. 1. The schematic of DMFC structure. 1 Anode electrode (azure blue) and anode active layer (red, 1 cm × 1 cm); 2 PFM; 3 cathode electrode, consisting of an active layer (blue, 1 cm × 1 cm), a gas diffusion layer (black) and a current accumulating matrix (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The structure and composition of the prepared KMn_8O_{16} powders were investigated with an X-ray diffractometer (XRD, Xpert-PRO, Holland) and energy-dispersive X-ray spectrometers (EDXS, OXFORD INCA300). The morphology of the samples was observed using field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan) and transmission electron microscopy (TEM, JEM-200CX, NEC, Japan). The Brunauer–Emmett–Teller (BET) surface areas and pore sizes of the as-prepared samples were measured using a nitrogen adsorption instrument (Micromeritics ASAP 2020).

2.2. Electrode preparation

The cathode for the DMFCs with PFM consisted of a gas diffusion layer, a current collector and an active layer. To prepare the gas diffusion layer, 60 wt.% acetylene black and 40 wt.% polytetrafluoroethylene (PTFE) (60 wt.% PTFE solution) with

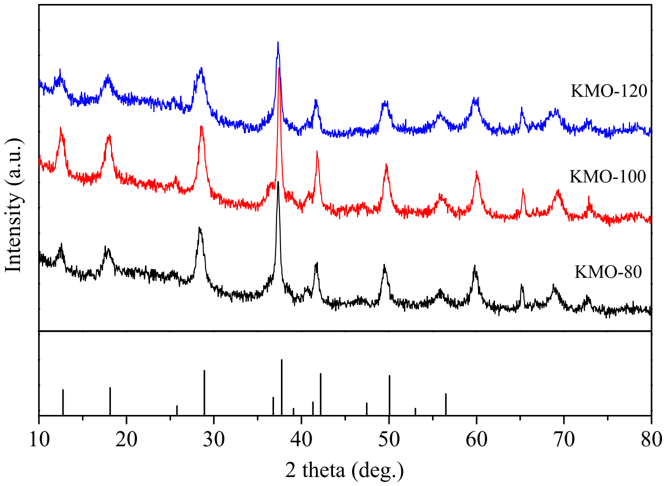


Fig. 2. XRD patterns for the KMO-80, KMO-100 and KMO-120 samples, respectively.