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MCM-41 as a new separator material for electrochemical cell: Application in zinc–air system

Hens Saputra, Raihan Othman*, A.G.E. Sutjipto, R. Muhida

Faculty of Engineering, International Islamic University Malaysia, P.O. Box 10, 50728 Kuala Lumpur, Malaysia

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ABSTRACT

The efficacy of nanoporous inorganic MCM-41 membrane as a new separator material for electrochemical cell has been investigated. The hexagonally ordered, narrow pore structure of MCM-41 membrane serves as ion exchange channels between the anolyte and catholyte of an electrochemical cell. Besides, it also acts as the electrolyte matrix or reservoir due to the hydrophilic nature of the as-synthesized MCM-41 and along with the high surface area and pore volume density characteristics. MCM-41 membrane has been employed as separator in zinc–air electrochemical system. MCM-41 was synthesized on the zinc substrate by dip-coating method and its thickness was ca. 5 μm. The Zn/MCM-41/air cell was able to produce a maximum power density of 32 mW cm^{-2} and possessed a volumetric energy density of 300 Wh l^{-1}, which are considered comparable to the published product datasheet of commercial zinc–air button cells of equivalent size.

1. Introduction

MCM-41 material belongs to a group of mesoporous materials known as M41S which was first reported by researchers of Mobil Research and Development Corporation in 1992 [1–3]. MCM-41 is characterized by its one-dimensional, hexagonally ordered pore structure; high specific surface area and pore volume of about 1000 m^2/g and 1 cm^3/g respectively; very narrow pore size distribution; tunable pore size between 1 nm to 10 nm or more depending on the choice of surfactant, auxiliary chemicals and reaction conditions; adjustable hydrophobicity; and very good thermal stability [1–3,5,6]. These properties are of considerable interest in the development of materials for electrochemical power sources [7].

In the present work, we investigated the efficacy of nanoporous inorganic MCM-41 membrane as a new separator material for an electrochemical cell. A separator in an electrochemical cell prevents an electronic contact between the anode and cathode, yet must be porous enough to allow ionic exchange between the anolyte and catholyte of the cell. MCM-41 possesses these properties. Its regular arrays of nano-channels shall provide the ion exchange pathways. Furthermore, it also acts as the electrolyte vehicle due to the hydrophilic nature of the as-synthesized MCM-41 and along with the high surface area and pore volume density characteristics. Polymeric membrane such as polypropylene and cellophane has been used almost exclusively as separator in commercial cells. However, they have poor wettability and often another absorbent layer (referred to as interseparator) such as nonwoven nylon or ALDEX [8] is needed as electrolyte reservoir, especially in compact cell design. Another setback of polymeric separator is its rapid degradation at elevated temperature operation. For cellophane separator as an example, high temperature operation is defined as over 55 °C [8]. MCM-41, on the other hand, has a very good thermal stability i.e. up to 900 °C [4–6].

In the succeeding sections, we shall present the synthesis and characterization of MCM-41 membrane, its application as the separator-cum-electrolyte matrix in a zinc–air electrochemical system. Popularly dubbed as *breathing batteries*, zinc–air or metal–air cells in general are unique in that they utilize oxygen from the ambient air as one of the electroactive materials. Hence this provides them with a practically unlimited and free oxygen supply. Further, the use of atmospheric oxygen does not require storage, which in principle reduces the weight and simplifies the cell design [9–14].

2. Experimental

2.1. Preparation of MCM-41 separator

MCM-41 separator on the zinc electrode was prepared using a dip-coating technique. The parent solution consisted

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* Corresponding author. Tel.: +60 3 61964561; fax: +60 3 61964853.
E-mail addresses: raihan@iiu.edu.my, raihan_othman@yahoo.com (R. Othman).

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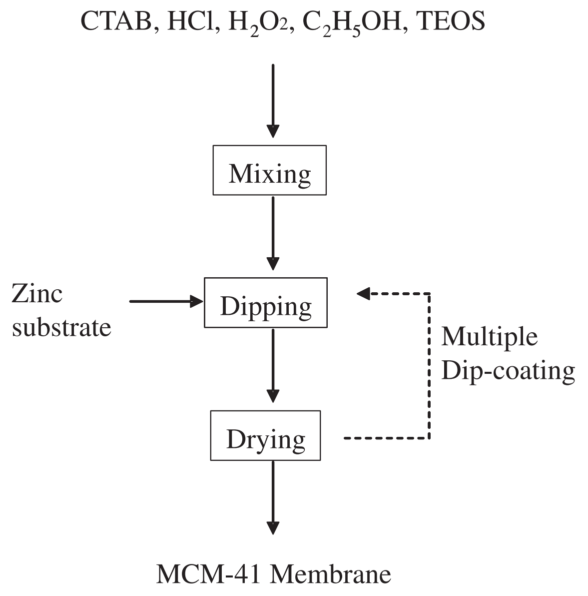

Fig. 1. Block diagram summarizing the preparation of MCM-41 membrane using dip-coating method.

of quaternary ammonium surfactant, cethyltrimethylammonium bromide $C_{16}H_{33}(CH_3)_3NBr$ ($C_{16}TAB$), hydrochloric acid, deionized water, ethanol, and tetraethylorthosilicate (TEOS) with molar ratio of 0.05 CTAB, 1.0 TEOS, 0.5 HCl, 25 C_2H_5OH and 75 H_2O. The mixture of parent solution was stirred at about 200 rpm at 30 °C for 1 h. Zinc substrate will then be dipped into the parent solution and dried. This procedure can be repeated to prepare membrane that will be thick enough to hinder the cracking or pinhole damage. One time dipping process results in MCM-41 film thickness of ca. 1 μm [15,16]. The procedures are summarized in a block diagram shown in Fig. 1.

2.2. Characterization of MCM-41

The structural verification of MCM-41 was conducted using X-ray diffraction (Cu Kα radiation, a scan range of 2–80 degrees 2θ and scan speed of 2 degree per minute). Its surface morphology and cross sectional micrograph were observed with Field-Emission Scanning Electron Microscope (FE-SEM) (JED-2100, JEOL Co. Ltd.) attached with an energy dispersive X-ray spectrometer (EDX) to analyze elemental composition. The BET surface area, pore volume and pore size distribution were analyzed using the Quantachrome AUTOSORB-1. MCM-41 powder sample was used. The sorption isotherms of nitrogen at 77 K were determined in a pressure range p/p^0 from 0.001 to slightly below 1.0.

2.3. Zn/MCM-41/air cell fabrication

2.3.1. Cell components

The anode was a zinc foil (99.9%, 250 μm thick), selected for ease of fabrication and rapid optimization. The cathode was a commercially available air electrode sheet which consists of laminated structures of fibrous carbon supported by a nickel-plated mesh. The air-side of the electrode was covered with a gas permeable, hydrophobic, Teflon layer. The whole structure was ca. 350 μm thick. An aqueous KOH electrolyte (3 M and 6 M) was employed. MCM-41 membrane served as the cell's separator as well as the electrolyte vehicle due to its hydrophilic characteristic. The planar structure of the Zn/MCM-41/air cell fabricated is schematically illustrated in Fig. 2. The cell dimension was 1 cm^2 area × ca. 600 μm thick.

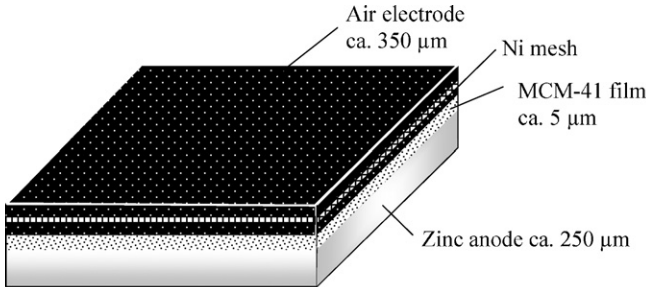

Fig. 2. Schematic drawing of Zn/MCM-41/air cell.

2.3.2. Electrodeposited zinc electrode

Zinc anode was also prepared from an electrodeposition process to obtain a high surface area electrode as the compact planar zinc foil might not demonstrate the actual cell performance due to its low surface area. An acidic sulphate plating bath with ammonium chloride supporting electrolyte was utilized. The counter electrode was a brass foil and the electrodeposited area was ca. 1 cm^2. Deposition current density was fixed at 100 mA cm^{-2} for duration of 3 h. The resulting zinc deposit weighed 0.35 g and ca. 100 μm thick.

2.3.3. Electrochemical characterizations

The fabricated cells employing MCM-41 separator were characterized according to their open circuit potential (OCV), polarization curve, power density profile and discharge capacity. An Eco Chemie (The Netherland) Autolab Galvanostat/Potentiostat was utilized to perform the measurements.

3. Results and discussion

MCM-41 material is characterized by a prominent X-ray diffraction plane of (1 0 0) (2θ∼2°) as shown in Fig. 3. In fact, the hexagonal lattice structure of MCM-41 is characterized by four peaks of $h\,k\,l$ (1 0 0) (1 1 0) (2 0 0) and (210) [1,17,18]. However the high intensity (1 0 0) diffraction normally suppressed the remaining peaks [15]. The FE-SEM cross sectional view as depicted in Fig. 4 indicates that thickness of MCM-41 coating on the zinc foil was ca. 5 μm. EDX elemental mapping further confirmed the formation of MCM-41 nanocomposite coating on the zinc substrate, as shown in Fig. 5. The white dotted region in Fig. 5(b) and (c) correspond to silicon and zinc elements respectively. Fig. 6 provides the quantitative element composition plot of the cross sectional area. The Si element peak is much less dominant than Zn due to the fact that MCM-41 layer was very thin compared to the zinc substrate and furthermore its structure was porous in nature. The FE-SEM image of the membrane surface at 200k magnification in Fig. 7 clearly reveals the porous nature and high surface area of the membrane.

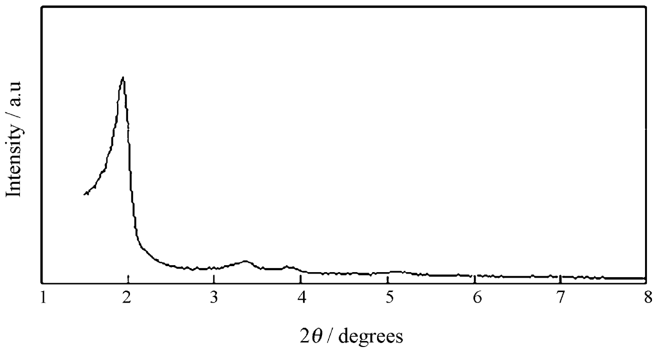

Fig. 3. XRD pattern of the as-synthesized MCM-41 confirming the existence of hexagonal lattice structure.