The viability of MCM-41 as separator in secondary alkaline cells

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Abstract. The viability of MCM-41 membrane as a separator material in secondary alkaline cell is investigated. The inorganic membrane was employed in an alkaline nickel-zinc system. MCM-41 mesoporous material consists of arrays of hexagonal nano-pore channels. The membrane was synthesized using sol-gel route from parent solution comprising of quaternary ammonium surfactant, ethyltrimethylammonium bromide $C_{16}H_{33}(CH_3)3NBr$ (CTAB), hydrochloric acid ($HCl$), deionized water ($H_2O$), ethanol ($C_2H_5OH$), and tetraethylortosilicate (TEOS). Both the anodic zinc/zinc oxide and cathodic nickel hydroxide electrodeposited film were coated with MCM-41 membrane. The Ni/MCM-41/Zn alkaline cell was then subjected to 100-cycle durability test and the structural stability of MCM-41 separator throughout the progression of the charge-discharge cycles is studied. X-ray diffraction (XRD) analysis on the dismantled cell shows that MCM-41 began to transform to lamellar MCM-50 on the 5th cycle and transformed almost completely on the 25th cycle. The phase transformation of MCM-41 hexagonal structure into gel-like MCM-50 prevents the mesoporous cell separator from diminished in the caustic alkaline surround. This work has hence demonstrated MCM-41 membrane is viable to be employed in secondary alkaline cells.

1. Introduction
The primary function of a separator is to provide physical barrier between the anode and cathode in order to prevent electrical short circuit. It also serves as electrolyte reservoir for the transport of ions during charge and discharge cycling of a battery [1]. Although a separator does not involve in chemical reactions of an electrochemical system, it has a direct influence on charge efficiency and discharge capacity of the cell. The wrong choice of separator may lead to premature cell failure [2].

The requirements of the separator often depend on the type of battery chemistry; for each chemistry has its typical cell behavior and concerns which need to be considered. In the case of lithium ion batteries for example, the separator should have very small pores and good mechanical strength to inhibit dendritic lithium penetration and conductive particles from the additives or active materials, in order to prevent short circuit and capacity loss [2]. The mechanical integrity of the separator should also remain preserved when the temperature rise during operation, i.e. its thermal shrinkage should be as low as possible [2]. As for Ni-Zn batteries, the separator should have the capability to lessen the solubility of zinc in the electrolyte to reduce capacity loss and the capability to protect the electrode from zinc dendrite penetration [1]. A separator for Ni-Zn battery typically consists of two different types and forms of materials i.e. wettable membrane (polypropylene and polyethylene) and nonwoven (polyamide) and is often constructed as multilayers [1-2].
Charging of Ni-Zn cell generates oxygen at the cathode. The oxygen needs to pass through the separator to reach the anode and recombine during discharge [2, 3]. Thus, it is essential that the separator to have a sufficient porosity for the mechanism to occur [2]. The gas evolution causes pressure buildup in the cell. Thus, the separator’s mechanical integrity needs to be unimpaired. The separator also needs to supply sufficient electrolyte for the transport of ions so that the cell reaction can occur, since water is produced during charging and is consumed during discharging [2]. Thus, its water retention capability should be high enough.

MCM-41 mesoporous material stands out due to characteristics of narrow pore size distribution, tunable pore sizes, extremely high surface area, high pore volume and adjustable hydrophobicity [4-7]. The structure consists of hexagonally ordered arrays of pore channels with uniform diameter. Its high water-adsorption affinity is due to the presence of silanol (Si-O-H) group at the pore walls [8]. Saputra et al. [9] first reported the use of MCM-41 as a separator in zinc-air cells. The cell performance was comparable with that of the commercial cell. They further reported the transformation of MCM-41 silica into gel-like MCM-50 after 24 hours of controlled exposure in 6-M KOH [10]. However, the studies were not conducted in a complete cell i.e. only the reaction between MCM-41 and KOH.

Herein, we study the structural stability of MCM-41 silica as separator in alkaline Ni-Zn secondary cell as the cell was subjected to 100 cycles of charge-discharge cycling. The cell was then dismantled after the progression of several cycles and the structural changes of the membrane analyzed using XRD.

2. Experimental Procedures

Cell Description and Process Flow. The experimental Ni-Zn secondary cell consisted of a zinc anode, nickel cathode, cell electrolyte and separator. The zinc anode comprised of a Zn foil coated with zinc oxide (ZnO) while the nickel cathode comprised of electrodeposited nickel hydroxide (Ni(OH)2) thin film on a copper substrate (of a blank printed circuit board (PCB)). A 6-M potassium hydroxide (KOH) solution was used as the electrolyte and MCM-41 silica thin film and powder were used as the separator. Three identical cells were prepared for the characterizations, in which each cell corresponded to different cycle number of charge-discharge cycling after which the separator material’s condition would be studied.

Synthesis of MCM-41 Silica Thin Film and Powder. Two forms of MCM-41 were used in the cell fabrication, i.e. thin film and powder. Sol-gel method was employed for the synthesis. The MCM-41 thin film was formed from the precursor solution. In a typical synthesis, the precursor solution was prepared by mixing a quaternary ammonium surfactant, cetyltrimethylammonium bromide (CTAB, CH3(CH2)15N(Br)(CH3)3; Merck, Germany) as an organic template, hydrochloric acid (HCl; J.T. Baker, Thailand), ethanol (C2H5OH; System) as a solvent, distilled water (H2O) and tetraethyl orthosilicate (TEOS, Si(OC2H5)4; Merck, Germany) as the silica source, with a molar ratio of 0.05 CTAB: 1.0 TEOS: 0.5 HCl: 25 C2H5OH: 75 H2O and stirring at 200 rpm, at a room temperature of 30 °C for about one hour [9]. On the other hand, the MCM-41 powder was synthesized by mixing CTAB, sodium hydroxide (NaOH, Sigma-Aldrich, Sweden), distilled water and TEOS, with a molar ratio of 0.05 CTAB: 1.0 TEOS: 0.5 NaOH: 100 H2O, and stirring at 200 rpm, heating the mixture on a hotplate at around 50 °C for 15 hours. The white precipitate of the MCM-41 powder was separated by filtration, rinsed with distilled water and dried at 100 °C.

Preparation of Zinc Anode. The Zn foil was prepared by successively grinding the surface of a Zn foil (2 cm x 1 cm) using P600 silicon carbide abrasive paper to obtain a new rough surface (free from oxide or grease), immersing (in a short time) in acetone and drying in ambient conditions. Subsequently, the Zn foil was dipped in a ZnO slurry (ZnO powder in ethanol). The ZnO-coated Zn was then let to dry at room temperature.
Preparation of Nickel Cathode. The nickel hydroxide (Ni(OH)$_2$) thin film was prepared by cathodic reduction (galvanostatically at current density of 8.5 mA/cm$^2$) of an electrolytic bath comprising 1.8-M nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O; Merck) (49.4 vol. %), 0.075-M sodium nitrate (NaNO$_3$; HmbG) (16.6 vol. %) and ethanol (34 vol. %). A nickel foil was used as the working electrode and copper substrate as the counter electrode. The dimensions of the effective area of the copper film were 2 cm x 1 cm and the distance between the electrodes was 2.3 cm. The electrodeposition was carried out for 75 minutes using an Autolab PGSTAT 302N (Eco Chemie B.V., Netherlands) potentiostat/galvanostat. The thin film formed on the surface of Cu was lightly rinsed with distilled water and then dried at room temperature.

Assembly of Cell Components.

The MCM-41 thin film was formed by drop-coating the as-synthesized MCM-41 precursor solution onto the surface of Ni(OH)$_2$ thin film using a pipette dropper. The solution would then self-spread over the entire surface of the thin film and left to dry at ambient conditions to form a layer of MCM-41 thin film. A total of 6 layers were prepared so as to obtain a firmly bonded Ni(OH)$_2$ thin film (to the surface of Cu substrate). The Ni(OH)$_2$ cathode and the Zn anode were then assembled into the cell casing (figure 1) and the gap in between the electrodes was filled with MCM-41 powder (0.35 g). The cell was activated by inserting KOH electrolyte (6 M, 0.5 ml) and finally sealed with acrylic resin.

Electrochemical Characterization. The cell was charged at a constant current of 2.0 mA for 2 hours, left at an open circuit potential for 5 minutes and then discharged at 0.2 mA until the cell potential reached 0.2 V. The steps were repeated for as many times until the cell was considered failed. A Neware battery testing system, model BTS-5V100mA (NEWARE Technology Ltd., China) was used.

Structural Stability Characterization. The main tool for the stability study was X-ray powder diffraction (XRD) and supported by surface morphology observation. A Bruker D8 ADVANCE X-ray diffractometer with a CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å), operating at 40 kV, 40 mA and a scan rate of 2.4 deg. 20/min was used for XRD measurement and a field emission scanning electron microscope (FE-SEM) model JEOL JSM-6700F was used for surface morphology observation. Prior to measurements, all samples were dried in a vacuum oven at 50 °C for 3-4 hours to ensure they were sufficiently dry.
3. Results and Discussion

XRD of MCM-41 and Ni(OH)$_2$ Materials. The presence of MCM-41 silica can be noted from the four low-angle peaks at 2.16°, 3.78°, 4.32° and 5.8° of 2θ, which can be indexed as (100), (110), (200) and (210) Bragg peaks, respectively, corresponding to the hexagonal ordered array. Figure 2 shows the XRD pattern of the as-prepared MCM-41 silica powder; the corresponding d-spacing values are also displayed in the figure. The XRD pattern confirms the typical mesoporous structure of MCM-41. From the XRD data, the repeat distance, $a_0$ between two pore centres in the MCM-41 is 4.72 nm ($a_0 = (2/\sqrt{3})d_{100}$), i.e. using the interplanar spacing $d_{100}$ value of 4.09 nm. The crystallite size of the MCM-41 powder based on the (100) plane, calculated from Scherrer’s equation is 20.9 nm.

![Figure 2 XRD pattern of the as-prepared MCM-41 silica powder.](image)

**Electrochemical Study of Ni-Zn Cell.** Figure 3 shows the charge-discharge cycling result of the Ni-Zn cell, i.e. discharge capacity profile as a function of cycle number. The result describes the electrochemical behaviour of the cell throughout the course. The first 13 cycles show the cell’s development or conditioning phase in which the capacity fluctuates prior to stabilizing i.e. up to the 13$^{th}$ cycle. Next, the cell underwent the mature phase (from the 14$^{th}$ to the 47$^{th}$ cycles) in which the cell capacity’s becomes stable as marked by the plateau region. Subsequently, from cycle-48 until cycle-68 the capacity started to decline monotonously. Finally in the failure phase, the capacity ceases towards zero, i.e. from the 69$^{th}$ cycle onwards. Based on the profile observed, the structural observation of the separator material was thus studied for the 5$^{th}$, 25$^{th}$ and 80$^{th}$ cycles of the development, mature and failure phases, respectively.

![Graph showing discharge capacity as a function of cycle number.](image)
**Figure 3** Discharge capacity profile of the Ni-Zn cell.

**XRD of the MCM-41 Separator.** Figure 4 shows the XRD patterns of the MCM-41 separator material for the 5th, 25th and 80th cycles (denoted as M5, M25 and M80, respectively). These XRD patterns denote the MCM-41’s transformation under the influence of KOH electrolyte and the cell’s charge-discharge conditions. From the results, the structural integrity of the membrane throughout the process can be analysed.

The peaks at 2θ of ca. 2.72° and 5.58° can be indexed to MCM-50’s (100) and (200) planes, respectively [11, 12]. All XRD patterns show the presence of MCM-50 peaks, suggesting that the lamellar phase is predominant in the separator materials. However, the XRD pattern of MCM-41 are also present in M5, i.e. the (100) peak, at 2.18° of 2θ, indicating that MCM-41 coexisted with MCM-50. The shift of the (100) peak of MCM-41 from 2.16° in the as-prepared sample to 2.18° in M5 implies the lattice contraction of the mesoporous silica and thus decreased pores size. Similar trend was observed in [10] but the authors did not make any remarks on the shift of (100) peak position of MCM-41 under KOH (10–30 wt.% loading effect. We attribute the lattice contraction to the formation of lamellar gel in the mix phase of MCM-50/MCM-41.

The (100) peak of MCM-41 is almost diminished in M25 and only a tiny peak appears at a substantially higher 2θ, i.e. 2.34° i.e. at this stage MCM-41 had almost entirely transformed to the lamellar MCM-50 phase. Whereas in M80, the predominant phase is MCM-50 and no trace of MCM-41 is observed.

Note that there are other peaks which are unindexed in M5 i.e. at 2θ of 3.06°, 3.38°, ~5.36°, ~6.1° and ~6.8°. Probably a transitional phase coexists with the diminishing two-dimensional (2D) hexagonal (p6mm) phase and the forming lamellar phase. These peaks are less distinct or absent in M25 and M80 samples.

**Figure 4** XRD patterns of the tested separator materials for different cycles.

Based on the XRD patterns of figure 4, it has been demonstrated that the MCM-41 membrane in the cell had partially underwent a phase transformation to MCM-50 as early as the 5th cycle and the material remained in the lamellar structure throughout the charge-discharge process. The phase transformation occurred as a result of the change of surfactant/silica molar ratio as the concentrated KOH reacts with the silica hexagonal matrix of MCM-41 [13]. This phenomenon prevented the collapse of the silica based separator material and hence the cell failure.

**Surface Morphology of the Gelled MCM-41 Separator.** The resulting formation of gelled MCM-41 (i.e. MCM-50) upon exposure to KOH was further inspected under the FE-SEM. The surface morphology of M5, figure 5(a), clearly indicates a particulate mixture morphology thus supporting the
existence of MCM-41 phase. After 25 cycles (M25), figure 5(b), the particulate morphology turned into homogeneous agglomerates which most likely was the gel formation. Finally in figure 5(c), after 80 cycles (M80) the surface smoothened. At this stage, the gel structure might have shrunk due to water loss. Water loss is as a result of electrolysis during charging and heat induced evaporation. These observations are in agreement with the interpretations of XRD results; M5 comprised the mixed MCM-41/MCM-50 phase, and, M25 and M80 comprised of lamellar MCM-50 phase.

Therefore, the capacity fading of Ni/MCM-41/Zn secondary cell is not attributed to the use of silica based separator that underwent transformation in caustic alkaline surround. In fact, the formation of lamellar gel of MCM-50 prevented the disintegration of separator material. The collapse of the separator would have short-circuited the cell which did not happen throughout the progression of the 100-cycle charge-discharge test.

![Figure 5 FE-SEM images of the separator materials which had gone through (a) 5, (b) 25 and (c) 80 cycles of charge-discharge cycling test.](image)

4. Conclusions

The viability of MCM-41 as separator in secondary alkaline cells has been demonstrated in Ni-Zn electrochemical system. Investigations on dismantled Ni-Zn cell at various stages of charge-discharge cycle substantiated the transformation of hexagonal silica network of MCM-41 into lamellar gel structure of MCM-50. This phenomenon prevented the collapse of silica separator material and it remained in the lamellar gel structure throughout the 100 cycles of deep charge-discharge durability test. The ultimate Ni-Zn cell failure or capacity loss was not attributed to the use of MCM-41 membrane separator but rather most likely due to the electrolyte drying out and the well-known problem associated with zinc electrode i.e. mobility of zinc discharge products.

References
[1] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu and X. Zhang, “A Review and Recent Developments in Membrane Separators for Rechargeable Lithium-Ion Batteries,” Energy Environ. Sci., 2014.
[2] P. Kritzter and J. A. Cook, “Nonwovens as Separators for Alkaline Batteries: An Overview,” J. Electrochem. Soc., vol. 154, no. 5, pp. A481–A494, 2007.
[3] M. Fetcenko, J. Koch and M. Zelinsky, “Nickel-Metal Hydride and Nickel-Zinc Batteries for Hybrid Electric Vehicles and Battery Electric Vehicles”. In B. Serosati, J. Garche and W. Tillmetz (Eds.), Advances in Battery Technologies for Electric Vehicles (pp.103-106), Cambridge: Woodhead Publishing, 2015.
[4] S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, “A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates,” J. Am. Chem. Soc., vol. 114, pp. 10834–10843, 1992.
[5] N. Nishiyama, S. Tanaka, Y. Egashira, Y. Oku, and K. Ueyama, “Vapor-Phase Synthesis of Mesoporous Silica Thin Films,” Chem. Mater., vol. 15, pp. 1006–1011, 2003.
[6] F. Hoffmann, M. Cornelius, J. Morell, and M. Fröba, “Silica-based Mesoporous Organic–Inorganic Hybrid Materials,” Angew. Chem. Int. Ed., vol. 45, pp. 3216–3251, 2006.
[7] M. Scheffel, N. Brodie–Linder, F. Audomnetx, and C. Alba–Simionesco, “Wall Thickness Determination of Hydrophobically Functionalized MCM-41 Materials,” J. Mater. Chem., vol. 22, pp. 557–567, 2012.
[8] J. C Vartuli, W. J. Roth, J. S. Beck, S. B. McCullen, and C. T. Kresge, “The Synthesis and Properties of M41S and Related Mesoporous Materials”. In H. G. Karge and J. Weitkamp (Eds.), Synthesis (Molecular sieves: Science and technology) (pp. 101 – 109), Berlin, Germany: Springer-Verlag Berlin Heidelberg, 1998.
[9] H. Saputra, R. Othman., A. G. E. Sutjipto, and R. Muhida, “MCM-41 as a New Separator Material for Electrochemical Cell: Application in Zinc-Air System,” J. Membr. Sci., vol. 367, no. 1–2, pp. 152–157, 2011.
[10] H. Saputra, R. Othman, A. G. E. Sutjipto, R. Muhida and M. H. Ani, “Gel-Like Properties of MCM-41 Material and Its Transformation to MCM-50 in a Caustic Alkaline Surround”, Mater. Res. Bull., vol. 7, pp. 732–736, 2012.
[11] A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurthy, P. Petroff, A. Firouzzi, M. Janicke, and B. F. Chmelka, “Cooperative Formation of Inorganic-Organic Interfaces in the Synthesis of Silicate Mesostructures,” Science, vol. 261 no. 5126, pp. 1299–1303,1993.
[12] F. Fajula, “Engineering of Mesostructured Silicas by Pseudomorphism,” Dalton Trans., pp. 291–294, 2007.
[13] J. C. Vartuli, K. D. Schmitt, C. T. Kresge, W. J. Roth, M. E. Leonowicz, S. B. McCullen, S. D. Hellring, J. S. Beck, J. L. Schlenker, D. H. Olson, and E. W. Sheppard, “Effect of Surfactant/Silica Molar Ratios on the Formation of Mesoporous Molecular Sieves: Inorganic Mimicry of Surfactant Liquid-Crystal Phases and Mechanistic Implications,” Chem. Mater., vol. 6, pp. 2317–2326, 1994.