



## Short communication

# Fabrication and electrochemical characterization of a vertical array of MnO<sub>2</sub> nanowires grown on silicon substrates as a cathode material for lithium rechargeable batteries

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## ABSTRACT

A complementary metal-oxide-semiconductor (CMOS) compatible process for fabricating on-chip micro-batteries based on nanostructures has been developed by growing manganese dioxide nanowires on silicon dioxide (SiO<sub>2</sub>)/silicon (Si) substrate as a cathode material for lithium rechargeable batteries. High aspect-ratio anodized aluminum oxide (AAO) template integrated on SiO<sub>2</sub>/Si substrates can be exploited for fabrication of a vertical array of nanowires having high surface area. The electrolytic manganese dioxide (EMD) nanowires are galvanostatically synthesized by direct current (dc) electrodeposition. The microstructure of these nanowire arrays is investigated by scanning electron microscopy and X-ray diffraction. Their electrochemical tests show that the discharge capacity of about 150 mAh g<sup>-1</sup> is maintained during a few cycles at the high discharge/charge rate of 300 mA g<sup>-1</sup>.

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## 1. Introduction

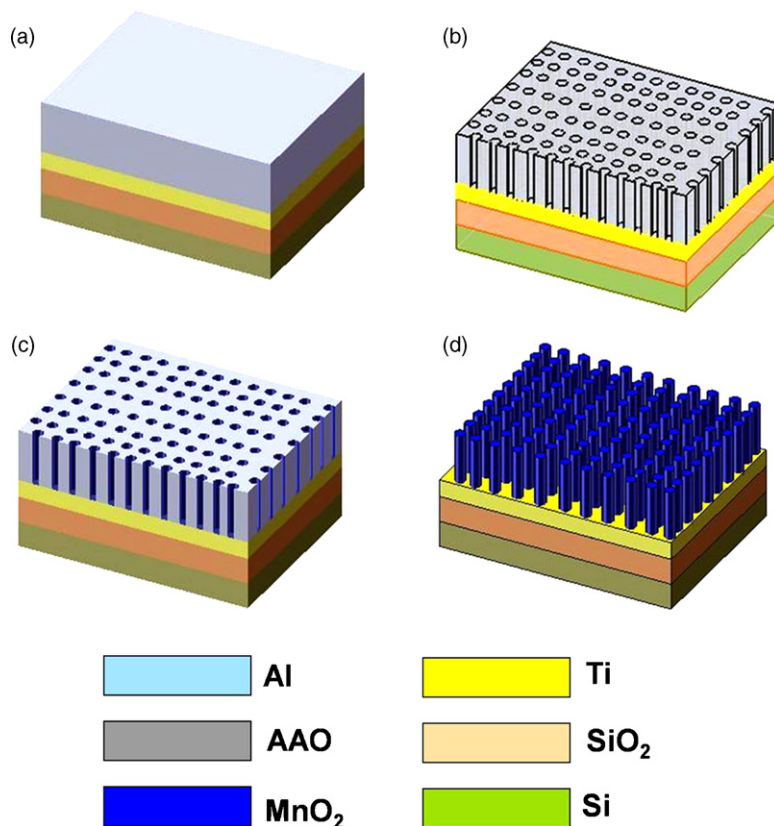
One-dimensional (1D) nanostructured materials have attracted wide attention due to their unique characteristics and extensive applications. While the aluminium foil process has allowed development of the key nanopore processing steps, for many practical applications it is necessary to produce 1D nanowire arrays on rigid substrates such as Si. In the field of lithium rechargeable batteries, many research efforts have been focused on nanosized materials for improving their electrochemical performances [1,2]. Manganese dioxides (MnO<sub>2</sub>) have received increasing attention for cathode materials in lithium ion batteries because of their structural variety as well as low cost and environmental friendliness [3–15].

The demands for thin film rechargeable batteries with a high rate capability and energy density are increasing for emerging applications like various electronic devices. The lack of a small, dependable and reliable power source has prevented many small electronic devices from reaching commercialization. The challenge has been to develop smaller and thinner rechargeable batteries for applications such as RFID tags, implanted medical devices, surveillance devices, etc. The use of nanostructured materials not only leads

to high rate capabilities as a result of high surface area but also because the smaller particle size leads to reduced diffusion distances [5–15]. In order to realize high surface area, various types of nanostructured materials have been developed by physical and chemical methods such as powder processing, a synthesis of free-standing nanowires, etc. However, these processes are not easy to be incorporated into complementary metal-oxide-semiconductor (CMOS) process for microbatteries on chips.

In this work, a process of fabricating vertical arrays of 1D manganese oxide materials on silicon chips has been developed using anodized alumina templates. The advantages of nanowire-based active materials are as follows: (1) 1D geometry of nanowires provides better accommodation of the large volume changes which results in improved cycle performance of the cathode materials [1]; (2) nanowires give a very large electrode surface area and surface to volume ratio to contact with electrolyte which provides conducting pathways for lithium ion and electron which enables efficient charge transport through the electrodes [1,2]. Thus these advantages can allow fast kinetics, which means improvement of the rate capability. Here we report the preparation and electrochemical properties of MnO<sub>2</sub> nanowires fabricated by electrodeposition which can provide superior performance, while utilizing a low-cost fabrication process. Since the nanowires are directly connected to the electrode which has a current collecting layer (titanium metal), the cathode can be fabricated without binders and conducting agent materials.

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**Fig. 1.** Schematic drawings showing the preparation of the vertical arrays of manganese dioxide nanowires grown on a silicon chip: (a) preparation of the Al/Ti/SiO<sub>2</sub>/Si wafer; (b) anodization of the aluminum layer; (c) electrodeposition of manganese oxide in the pores of the alumina template; (d) etching to remove the alumina template.

## 2. Experimental

### 2.1. Preparation of manganese oxide nanowires on Si chips

The fabrication of vertical arrays of MnO<sub>2</sub> nanowires on SiO<sub>2</sub>/Si substrates consists of the following steps as shown in Fig. 1: (a) first, 1 μm thick aluminum layer was deposited on a SiO<sub>2</sub>/Si substrate using a sputtering method; (b) anodization (anodic oxidation) of the aluminum layer was carried out in 0.3 M oxalic acid at a constant voltage of 20 V. This process initiates growth

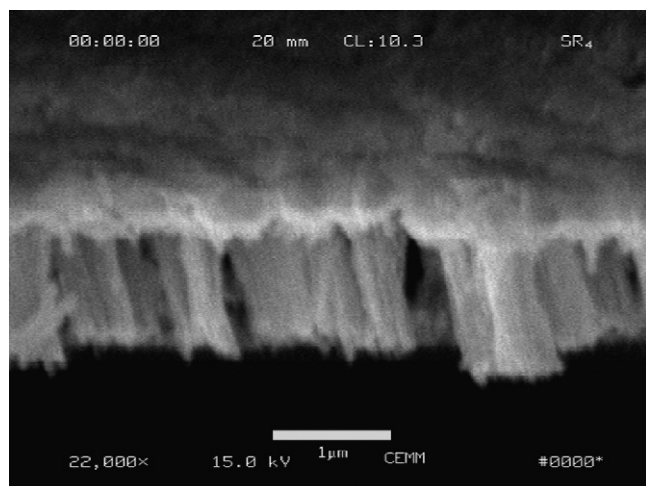
of cylindrical pores from surface of Al film. Hexagonal-shaped ordered arrays of alumina nanopore templates with uniform size cylindrical pores can be resulted from this process. Pore dimensions of 10–200 nm can be controlled by anodizing conditions; (c) anodic electrodeposition was performed to grow about 1 μm long MnO<sub>2</sub> nanowires in the alumina pores. MnO<sub>2</sub> nanowires were galvanostatically electrodeposited in a bath prepared by mixing 1 M MnSO<sub>4</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub> at a constant current density of 5 mA cm<sup>-2</sup> using potentiostat/galvanostat model 760C of CH Instruments; (d) finally, wet etching for removal of the alumina template layer with 1 M NaOH was carried out to realize exposed vertical arrays of MnO<sub>2</sub> nanowires on a SiO<sub>2</sub>/Si substrate. Electrochemically deposited manganese dioxide (electrolytic manganese dioxide, EMD) contains certain amount of water molecules incorporated during electrodeposition [3]. The MnO<sub>2</sub> nanowire array electrode was heat-treated at 350 °C for 1 h to minimize the amount of water contents in MnO<sub>2</sub> nanowires.

### 2.2. Material characterization of the nanowire samples

The obtained samples were investigated using X-ray diffraction (XRD, Bruker/Siemens SMART APEX diffractometer with Mo Kα radiation, λ = 0.71073 Å). The morphology, microstructure and composition of the prepared samples were examined by scanning electron microscope (SEM, Amray 1830) attached with energy dispersive X-ray spectroscopy (EDS).

### 2.3. Electrochemical measurements

A vertical array of manganese oxide nanowires grown on a SiO<sub>2</sub>/Si substrate was used as a working electrode which is elec-



**Fig. 2.** SEM micrograph of the vertical array of manganese dioxide nanowires grown on a silicon chip (scale bar: 1 μm).

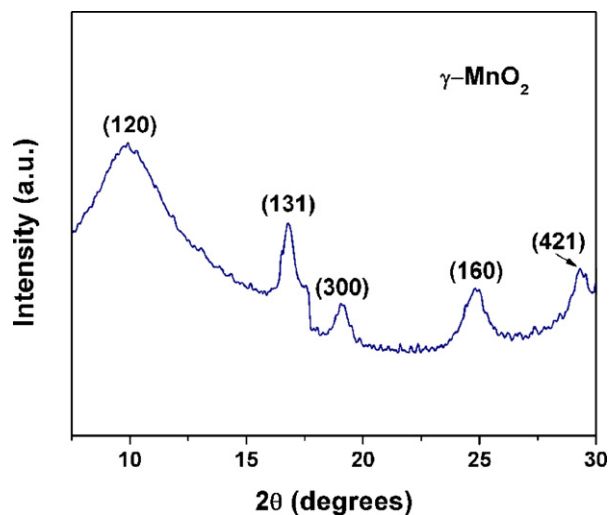


Fig. 3. XRD pattern of the electrolytic manganese dioxide prepared by an anodic electrodeposition technique. Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was used.

trically connected by an aluminum foil current collector. Coin-type test cells were assembled in an Ar-filled glove box using Celgard 480 as a separator, 1 M LiPF<sub>6</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 volume ratio, Aldrich) as an electrolyte and Li foil (Alfa Aesar) as a counter electrode and a reference electrode. The discharge (Li insertion into the working electrode)–charge (Li removal) experiments were performed galvanostatically within the voltage window of 2.0–3.9 V (vs. Li/Li<sup>+</sup>).

### 3. Results and discussion

When the aluminum thin film layer is anodized in the oxalic acid, aluminum becomes a porous aluminum oxide which has uniform and parallel arrays [16]. The porous anodized aluminum oxide has been used to fabricate various materials for electronic, optical, and energy devices since Masuda et al. reported the periodic pore arrangement in porous anodic alumina [17–21]. The SEM image of nanowire shaped manganese oxide grown on a silicon chip is presented in Fig. 2. To produce MnO<sub>2</sub> nanowires extending out of the nanopores in anodized aluminum oxide (AAO) templates, the top surface of alumina is typically etched back using wet etching to remove the aluminum oxide. However, it has been found that the exposed nanowire ends often stick together to minimize the free energy in the system after this etching process as shown in Fig. 2, which shows the cross section of the EMD nanowires after etching in 1 M NaOH for 10 min. Although the nanowires resulted from etching do not maintain ordered and vertical arrays on a substrate, surface area of the MnO<sub>2</sub> cathode material is found to be increased by dense arrays of MnO<sub>2</sub> nanowires. In this figure, the vertical nanowire arrays are clearly observed and their diameters are ranged between 50 and 100 nm. The length and the diameter of the MnO<sub>2</sub> nanowires correspond to those of the nanopores in the AAO template. The EDS measurement revealed that the oxygen/manganese ratio is near 2 with trace of impurities from the electrolyte for electrodeposition and etching solution.

Fig. 3 shows the XRD pattern of the electrolytic manganese dioxide. All of the peaks observed can be assigned to  $\gamma$ -MnO<sub>2</sub> phase (ICDD-JCPDS No. 14-0644,  $a = 6.36 \text{ \AA}$ ,  $b = 10.15 \text{ \AA}$  and  $c = 4.09 \text{ \AA}$ ) which is typically found in the EMD [3,5]. The broad diffraction peaks indicate the manganese dioxide sample is not well crystallized, which can drive the high capacity of EMD for lithium battery application [5].  $\gamma$ -MnO<sub>2</sub> has an intergrowth structure

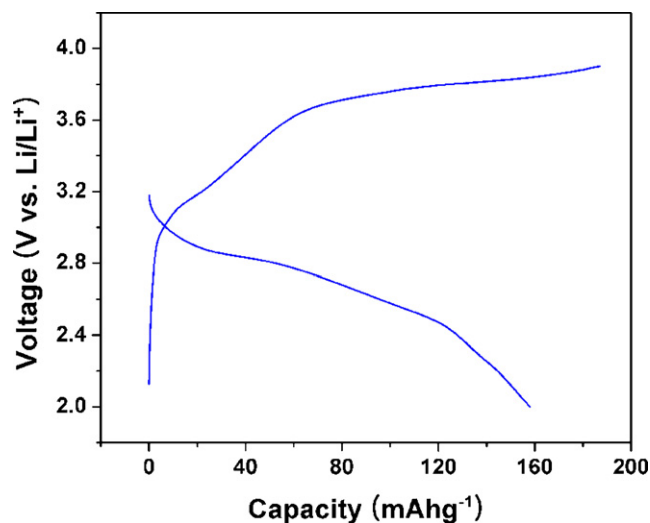


Fig. 4. Voltage profiles of the manganese dioxide nanowire electrode cycle in the voltage region of 2.0–3.9 V at a constant current of  $150 \text{ mA g}^{-1}$  (=1 C rate).

which contains  $\beta$ -MnO<sub>2</sub> domains of relative size (1  $\times$  1), and ramsdellite-MnO<sub>2</sub> domains of size (2  $\times$  2). After annealing,  $\beta$ -MnO<sub>2</sub> becomes predominant, whose phase has only narrow one-dimensional channels for lithium ion diffusion [3,5]. Therefore, less crystalline EMD would be suitable for lithium batteries in terms of short diffusion path for lithium ions.

Fig. 4 presents voltage profiles for the first discharge and charge curves of the vertical arrays of manganese oxide nanowires grown on a SiO<sub>2</sub>/Si substrate and subsequently annealed at 350 °C as a cathode in the voltage region of 2.0–3.9 V at a constant current of  $150 \text{ mA g}^{-1}$  (=1 C rate). The first discharge capacity is about  $160 \text{ mAh g}^{-1}$ , which can be obtained from normal EMD materials [3]. During the first discharge process, smooth voltage profile is observed and it implies that lithium ions are inserted into the less crystalline tunnel structure of  $\gamma$ -MnO<sub>2</sub>. Thus, it is believed that the EMD nanowires prepared in this study would be suitable for use as a cathode for lithium batteries.

The cycle performances of the EMD nanowire grown electrodes cycled at different rates of  $150 \text{ mA g}^{-1}$  (=1 C) and  $300 \text{ mA g}^{-1}$  (=2 C) are compared in Fig. 5. At the high discharge/charge rate of  $300 \text{ mA g}^{-1}$ , it is found that the discharge capacities of about

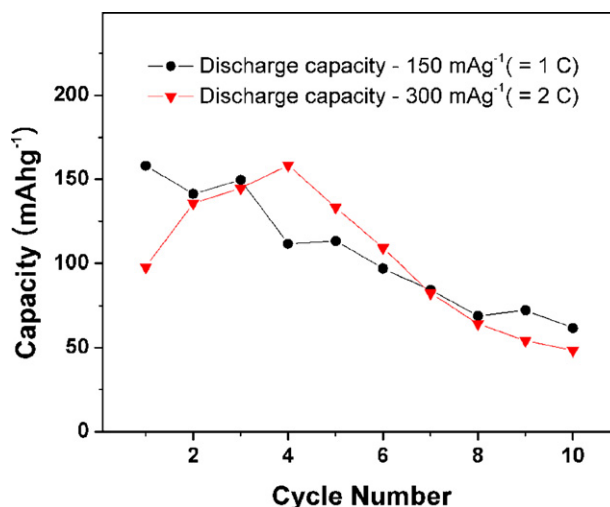


Fig. 5. Cycle performances of the manganese dioxide nanowire electrodes cycled at the constant currents of  $150 \text{ mA g}^{-1}$  (=1 C) and  $300 \text{ mA g}^{-1}$  (=2 C), respectively.

150 mAh g<sup>-1</sup> are still maintained during a few cycles. It can be attributed to the high-surface-area of 1D MnO<sub>2</sub> nanowires, which can provide more active sites for the contact between the electrode material and electrolyte [1,2,15]. However, the discharge capacity fades upon more cycling. It might be resulted from the fact that the hexagonally close-packed arrangement of  $\gamma$ -MnO<sub>2</sub> is distorted during lithium repeated insertion and extraction [3]. Currently, we are investigating this topic to improve the cycle performances of EMD nanowire electrodes.

#### 4. Conclusions

A vertical array of MnO<sub>2</sub> nanowires grown on SiO<sub>2</sub>/Si substrates was prepared using high aspect-ratio anodized aluminum oxide templates and a subsequent anodic electrodeposition. This fabrication process is expected to be very reliable, cost effective, and CMOS-compatible. The EMD nanowires are demonstrated to function as a cathode material for lithium rechargeable microbatteries. The EMD nanowire electrode having high surface area enables realizing multiple discharge/charge cycling with a specific capacity of about 150 mAh g<sup>-1</sup> as a cathode even at a high rate of 300 mA g<sup>-1</sup>.

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#### References

- [1] C.K. Chan, H. Peng, G. Liu, K. Mcllwraith, X.F. Zhang, R.A. Huggins, Y. Cui, *Nat. Nanotechnol.* 3 (2008) 31–35.
- [2] D.-W. Kim, I.-S. Hwang, S.J. Kwon, H.-W. Kang, K.-S. Park, Y.-J. Choi, K.-J. Choi, J.-G. Park, *Nano Lett.* 7 (2007) 3041–3045.
- [3] M.M. Thackeray, *Prog. Solid State Chem.* 25 (1997) 1–71.
- [4] M.S. Whittingham, *Chem. Rev.* 104 (2004) 4271–4301.
- [5] H. Kurimoto, K. Suzuoka, T. Murakami, Y. Xia, H. Nakamura, M. Yoshio, *J. Electrochem. Soc.* 142 (1995) 2156–2162.
- [6] G. Amatucci, J.-M. Tarascon, *J. Electrochem. Soc.* 149 (2002) K31–K46.
- [7] M. Nishizawa, K. Mukai, S. Kuwabata, C.R. Martin, H. Yoneyama, *J. Electrochem. Soc.* 144 (1997) 1923–1927.
- [8] N. Li, C.J. Patrissi, G. Che, C.R. Martin, *J. Electrochem. Soc.* 147 (2000) 2044–2049.
- [9] C.S. Johnson, *J. Power Sources* 165 (2007) 559–565.
- [10] P. Liu, S.-H. Lee, Y. Yan, C.E. Tracy, J.A. Turner, *J. Power Sources* 158 (2006) 659–662.
- [11] W. Bowden, T. Bofinger, F. Zhang, N. Iltchev, R. Siroтина, Y. Paik, H. Chen, C. Grey, S. Hackney, *J. Power Sources* 165 (2007) 609–615.
- [12] T. Ohzuku, R.J. Brodd, *J. Power Sources* 174 (2007) 449–456.
- [13] W.C. West, N.V. Myung, J.F. Whitacre, B.V. Ratnakumar, *J. Power Sources* 126 (2004) 203–206.
- [14] M.M. Doeff, A. Anapolsky, L. Edman, T.J. Richardson, L.C. De Jonghe, *J. Electrochem. Soc.* 148 (2001) A230–A236.
- [15] F. Cheng, J. Zhao, W. Song, C. Li, H. Ma, J. Chen, P. Shen, *Inorg. Chem.* 45 (2006) 2038–2044.
- [16] N.V. Myung, J. Lim, J.-P. Fleurial, M. Yun, W. West, D. Choi, *Nanotechnology* 15 (2004) 833–838.
- [17] H. Masuda, K. Fukuda, *Science* 268 (1995) 1466–1468.
- [18] K. Nielsch, F. Muller, A.-P. Li, U. Gosele, *Adv. Mater.* 12 (2000) 582–586.
- [19] H. Masuda, K. Kanazawa, M. Nakao, A. Yokoo, T. Tamamura, T. Sugiura, H. Minoura, K. Nishio, *Adv. Mater.* 15 (2003) 159–161.
- [20] M.S. Sander, A.L. Prieto, R. Gronsky, T. Sands, A.M. Stacy, *Adv. Mater.* 14 (2002) 665–667.
- [21] Y. Zhou, C. Shen, J. Huang, H. Li, *Mater. Sci. Eng. B* 95 (2002) 77–82.