

Short communication

# Electrodeposited amorphous manganese oxide nanowire arrays for high energy and power density electrodes

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## Abstract

Arrays of manganese oxide nanowires were electrodeposited into anodized alumina membranes. These nanowire arrays were investigated in terms of their structural and electrochemical properties as cathodes for high energy and high power density Li ion batteries. The nanowire arrays were assembled with a Li counter electrode and non-aqueous electrolyte to form secondary batteries. These cells were capable of multiple charge/discharge cycles, with a cathode specific capacity of approximately 300 mA h/g. Though the cathodes were fabricated without any binder or conductive additives, the electrodes could be discharged at current densities up to 0.1 mA/cm<sup>2</sup> before the onset of any significant polarization.

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## 1. Introduction

The power density of a lithium ion cell is dictated, at the fundamental level, by the electrochemical kinetics of charge transfer at the electrode/electrolyte interface and the kinetics of solid-state diffusion of lithium ions into and out of the host electrodes. Thus, the rate capability of battery electrodes is highly dependent on the grain size, texture, surface area, and morphology of the electrode materials. The ability to engineer an ordered, large surface area structure of electrochemically active materials on the nanoscale can yield enhanced charge/discharge characteristics. For example, other groups have demonstrated that high surface area nanowire electrodes of SnO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> have significantly improved rate capability compared with thin films of the same material [1–3]. Nanostructured electrodes of V<sub>2</sub>O<sub>5</sub> delivered four times the capacity of a V<sub>2</sub>O<sub>5</sub> thin film electrode at discharge rates of 500 °C [3]. In addition, the synthesis of nanowire electrode arrays results in electrodes without any binders or conductive additives, other than the thin film substrate support which is typically no more than 200 nm of vacuum-deposited metal. This electrode design results in improvements in elec-

trode energy density compared with conventional lithium ion cathodes that use up to 10% binder and 20% carbon black.

However, in order for nanowire materials to be used as viable electrodes in battery cells, the fabrication process must be amenable to scale-up. Thus, we investigated various materials and deposition schemes to fabricate nanowire electrodes. One suitable candidate material is amorphous manganese oxide, which can be readily electrodeposited over large areas. This material has been reported to very good specific capacity of between 160 and 350 mA h/g, and can function as a secondary lithium battery cathode despite in some cases the presence of water and alkali metal ions within the amorphous manganese dioxide [4–7].

In this study, we have electrodeposited nanowire arrays of amorphous manganese oxides, constructed lithium battery cells using the nanowire arrays as the cathode, and have demonstrated multiple charge and discharge cycles between 3.1 and 2.0 V. These nanowire electrodes consist of only electrochemically active material (manganese oxide), and have no binder or conductive additives.

## 2. Experimental

The manganese oxide nanowire arrays were electrodeposited into commercially available alumina membranes

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(Whatman Anodiscs, diameter = 13 or 25 mm) with pore diameters of approximately 200 nm, with an estimated porosity of 43%. The alumina nanotemplates were sputter-coated on one side with a Au film approximately 200 nm thick, and were mounted onto Au coated Si substrates with Ag or C paste. The substrates were carefully masked with tape to allow electrodeposition to occur only within the template and not on the Si substrate.

The manganese oxide nanowire arrays were synthesized using two different electrodeposition approaches. The first approach was deposition via potentiostatic control with applied potential varied between 0.2 and 1.2 V versus SCE in an alkaline manganese sulfate room temperature bath. The bath consisted of an aqueous solution of 0.01 M  $\text{MnSO}_4$  with 0.03 M  $(\text{NH}_4)_2\text{SO}_4$  as a complexing agent, maintained at a pH of 8 through the addition of  $\text{H}_2\text{SO}_4$  or  $\text{NH}_4\text{OH}$ . Other groups have shown that by controlling the electrodeposition potential for this bath chemistry, the valence of the manganese in the electrodeposit can be tailored between mixtures of the divalent–trivalent and trivalent–tetravalent states [8]. The second deposition approach was the more conventionally employed manganese oxide deposition bath consisting of 1 M  $\text{MnSO}_4$  and 0.5 M  $\text{H}_2\text{SO}_4$ , with galvanostatic control set to 10 mA/cm<sup>2</sup> at room temperature.

After electrodeposition, the alumina membranes were digested by immersing the samples in a 1 M NaOH solution for about 6 h, and then the samples were soaked in de-ionized water for 6 h, and then were air dried roughly 24 h. No elevated temperature drying was attempted in order to avoid disrupting the as-deposited amorphous state of the manganese oxide. It should be noted that although the focus of this study was to demonstrate secondary battery cathodes, by simply annealing the nanowires at approximately 350 °C, the amorphous manganese oxide could readily be converted to crystalline  $\text{MnO}_2$ , which could function as a primary cathode material.

The nanowire arrays were then characterized for morphology, composition, and crystallography. Surface morphology was studied using a Hitachi field-emission scanning electron microscope (SEM) and compositional analysis was studied by X-ray energy dispersive spectroscopy (EDS). The EDS data was collected on a Cambridge Stereoscan (LaB6 filament) SEM using an IXRF model 500 energy dispersive detector. Sample crystallography characterization was performed at the Stanford Synchrotron Radiation Laboratory (SSRL). To maximize the scattered signal, the asymmetric GIXS geometry was used on beamline 2-1 at SSRL (3 GeV and 100 mA at fill) [9]. A silicon (1 1 1) monochromator was used to select the wavelength of the X-ray beam, 0.154996 nm, in focused mode. Diffracted X-ray intensity was measured using a standard scintillation counter. Samples were manipulated using an automated Hüber two-circle diffractometer that was controlled using a UNIX workstation. All measurements were conducted using a set dose for each data point, eliminat-

ing any possible experimental error due to beam intensity fluctuation.

After confirming the electrodeposits were amorphous manganese oxide, electrochemical test cells were constructed using the nanowire arrays. The cathode terminals were the freestanding manganese oxide nanowires deposited on the Au current collector, mounted on the Au coated Si substrate. The anodes were Li foil pressed onto Ni mesh, and the electrolyte was 1 M  $\text{LiPF}_6$  in propylene carbonate or 1 M  $\text{LiPF}_6$  in a 1:1:1 volumetric ratio solution of dimethyl carbonate:ethylene carbonate:diethyl carbonate (Mitsubishi Chemicals). The cells were charged at different cutoff voltages and current taper durations in attempts to maximize capacity and minimize irreversible capacity losses. The charge cutoff voltage range was between 3.8 and 4 V, while the discharge cutoff voltage was limited to 2.0 V.

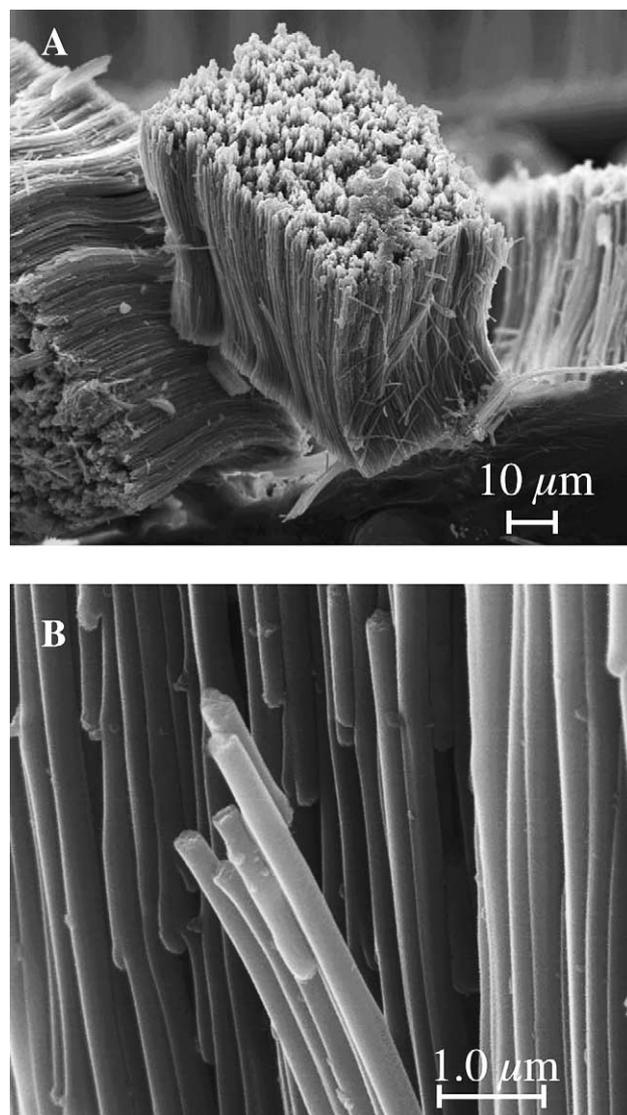


Fig. 1. SEM micrographs of manganese oxide nanowire arrays fabricated by potentiostatic electrodeposition: (A) 1000× magnification and (B) 20,000× magnification.

### 3. Results and discussion

Nanowire arrays from the first electrodeposition approach are shown in Fig. 1, and nanowire arrays from the second method are shown in Fig. 2. All characterization aside from the microscopy studies was performed on samples of manganese oxide nanowires prepared by the latter method since this approach appeared to yield the most consistent electrodeposits. Use this deposition scheme resulted in nanowires approximately  $6.5\ \mu\text{m}$  in length after 3 h of deposition at  $10\ \text{mA}/\text{cm}^2$ . The EDS measurements showed that the O/Mn stoichiometric ratio was  $2.2 \pm 0.1$ . Care should be taken in interpreting these results, given the possibility of differing stoichiometry at the interior and exterior of the nanowires. Whereas the contribution of surface species to the stoichiometric ratio measured by EDS may be very small for thin film samples, the role of the surface chemistry for the nanowire samples is much greater given the significantly larger surface area. Trace amounts of Na were also observed, the presence of which can be attributed to incomplete nanowire rinsing following the template dissolution step.

As deposited, the nanowires were fully amorphous, as determined by synchrotron X-ray diffraction patterns, shown in Fig. 3. No reflections were discerned other than the Au (111) peak from the nanowire Au contact layer. This result was consistent with other reports of as-deposited amorphous manganese oxide films [4], but bears note since the synchrotron X-ray diffraction measurement is far more sensitive than conventional laboratory X-ray diffraction instruments in discerning any nanocrystalline structure.

The nanowire arrays were easily assembled into functional electrodes for Li battery cells. The cells could tolerate reasonably high current density, despite the lack of any binder or conductive diluent in the cathode. Fig. 4 shows

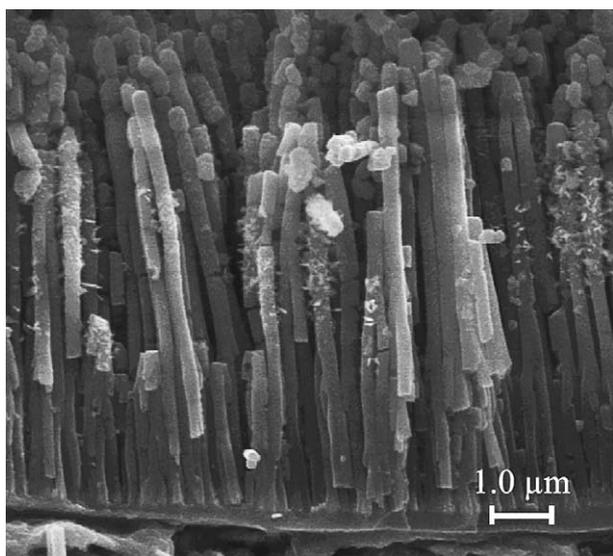


Fig. 2. SEM micrograph of manganese oxide nanowire arrays fabricated by galvanostatic electrodeposition ( $13,000\times$  magnification).

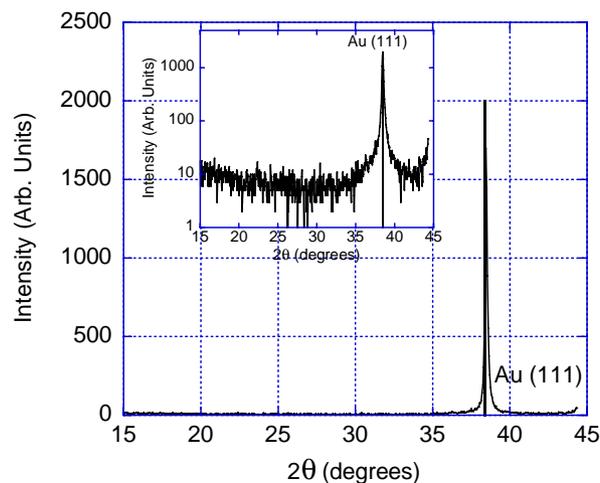


Fig. 3. Synchrotron X-ray diffraction pattern of manganese oxide nanowires on a Au film current collector prepared by galvanostatic electrodeposition. The inset shows the same data plotted using a logarithmic scale for the intensity.

the Tafel polarization behavior of the charged cells, which could discharge at up to  $100\ \mu\text{A}/\text{cm}^2$  before the onset of significant cell polarization.

The electrochemical cells were capable of multiple charge and discharge cycles. The data from a representative charge/discharge cycle is shown in Fig. 5. The cycles were characterized by irreversible capacity on every cycle, depending on the charge cutoff voltage and current taper duration. Different charge cutoff voltages had limited effect on the discharge capacity, though higher charge cutoff voltage resulted in poorer irreversible capacity performance, as shown in Fig. 6. On cycling, some gas evolution was observed at the cathode regardless of electrolyte solvents or charge cutoff voltage, which resulted in frequently uneven charge/discharge profiles as the gas bubbles desorbed from the electrodes. The gas evolution increased with increasing

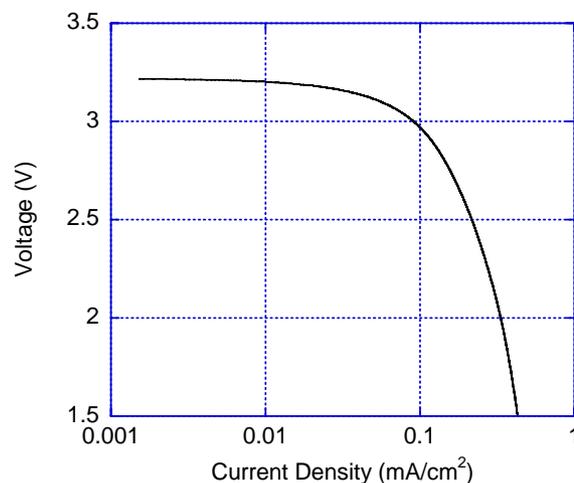


Fig. 4. Tafel polarization plot of a manganese oxide nanowire cathode [ $1.0\ \text{M LiPF}_6$  in PC] Li/Li<sup>+</sup> cell.

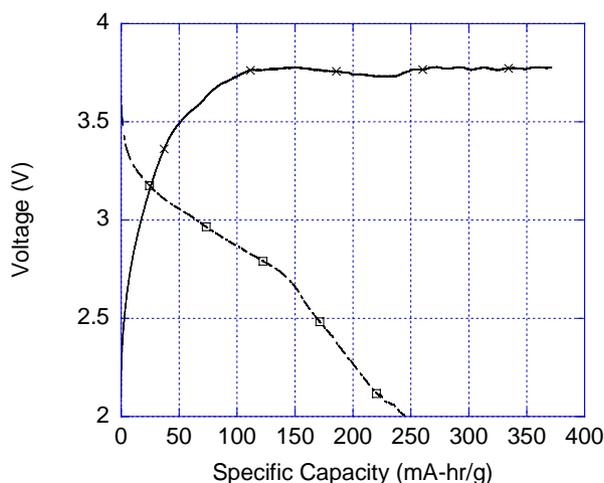


Fig. 5. Representative charge/discharge curves, at  $50 \mu\text{A}$  for a  $1.33 \text{ cm}^2$  cathode active area.

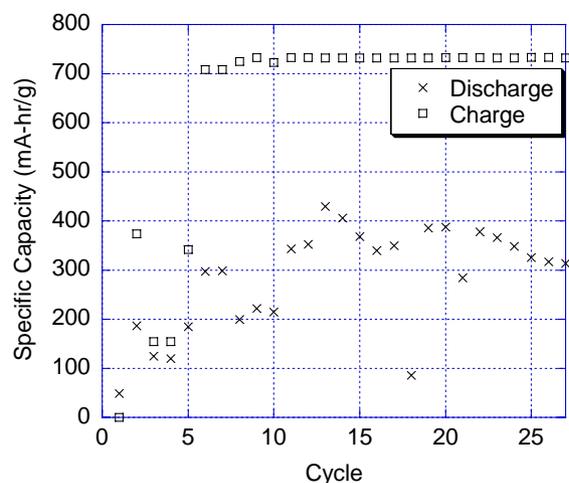


Fig. 6. Charge/discharge capacity as a function of cycle. The first three cycles were conducted with a charge cutoff voltage of 3.8 V, while the remaining cycles were charged to a cutoff voltage of 4.0 V.

cycle number, so that an accurate measurement of capacity fade as a function cycle was not possible. Nonetheless, the cells were charged and discharged tens of times with apparently minimal capacity loss.

The appearance of gas bubbles at the cathode suggests an undesirable side reaction. Although no quantitative analysis of the moisture content of the cathode was performed, based on literature reports of unannealed electrodeposited manganese oxide [4,8], we expect that the nanowire matrices contain both adsorbed water as well as “structural” water molecules within the amorphous manganese oxide. The adsorbed water molecules will very likely react upon lithiation of the cathode to form lithium oxide or lithium hydroxide thus leading to irreversible capacity loss. Though vacuum

annealing would remove the residual water from the cathode, this would potentially destroy the structure of the hydrated manganese oxide nanowires. Other groups have shown that the interlayer structural water molecules within lamellar hydrated  $\text{MnO}_2$  are important for affording reversible Li insertion, see for example [10]. Additional work is warranted to minimize the amount of weakly absorbed water while not disturbing the more tightly bound structural water molecules.

#### 4. Conclusions

Arrays of freestanding nanowires were prepared by potentiostatic electrolysis and anodic electrodeposition of manganese oxide in nanoporous alumina templates. The nanowire arrays were shown to function as rechargeable cathodes for Li battery cells, with discharge potentials from 3.5 to 2 V. These cells were capable of multiple charge/discharge cycles, with specific capacity of the cathode approximately 300 mA h/g. Though the cathodes were fabricated without any binder or conductive additives, the electrodes could be discharged at current densities up to  $0.1 \text{ mA/cm}^2$  before the onset of any significant polarization.

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