Supporting Information

Reversible Anomalous High Lithium Capacity for MnO₂

Nanowires

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Experimental

Synthesis of freestanding MnO₂ nanowire array

First, a Denton Desk III sputter machine is used to sputter a ≈ 300 nm gold layer on the branched side of an AAO membrane. In order to provide good electrical contact, a strip of copper tape is attached to the gold side of the membrane. This piece is then sandwiched between layers of Parafilm with a portion of the non-sputtered side exposed to the electrolyte with a defined window of 0.32 cm² resulting in completion of the working electrode.

The working electrode is then placed in a 100 mM manganese acetate bath with a Ag/AgCl reference and a platinum counter electrode. A constant voltage of 0.60 V vs. Ag/AgCl is applied until 150 mC of charge was charge passed. This is followed by a soaking time of 15 minutes in a 3 M solution of sodium hydroxide in order to completely dissolve the alumina membrane. This results in a working electrode consisting of vertically aligned MnO_2 nanowire arrays attached to a gold current collector.

Electrochemical Analysis

After the chemical dissolution of the template, MnO_2 nanowire arrays are soaked in DI water twice for five minutes in order to remove any residual hydroxide. The arrays are then placed in either water or acetonitrile, depending on their analytical solvent, and soaked again for five minutes. Finally, the arrays are placed in their test solution (0.1 M LiClO₄ in either water or acetonitrile).

For the galvannostatic testing, the nanowires are galvanostatically scanned from 0 to 1 V vs. Ag/AgCl at a 1 A/g current density and stopped at specific voltages. For the holding potential test, a specified voltage vs. Ag/AgCl is applied for 15 minutes. There was no significant change in the lithiation amount when the material was initially held at 1.0 V and then held at the specific voltage; therefore, all holding potential experiments were initially at open circuit potential before applying the specified voltage unless otherwise stated.

After testing, the arrays are soaked in either DI water or pure acetonitrile three times for five minutes

each. This is done in order to avoid any contamination from the high concentration lithium salt in the testing solution. After soaking, the electrodes are ready to be dissolved and administered to the ICP-AES instrument.

Inductive coupled plasma – atomic emission spectroscopy (ICP-AES)

All electrodes are dissolved in 3:1 concentrated HCI:HNO3 and diluted to a known volume before being administered to the plasma.

ICP-AES measurements were performed using a PerkinElmer ICP-Optima 4300. Intensities are measured at 257.610 nm for Mn and 670.784 nm for Li. Calibration curves are made from Mn and Li standards traceable to the National Institute of Standards and Technology (NIST).

Raman Spectroscopy

Raman measurements are performed on electrodes held at diiferent potentials in lithiated acetonitrile solvents. A Horiba Jobin-Yvon LabRAM HR-VIS microRaman system is used to characterize these manganese oxide materials. The green line (514.5 nm) of an argon laser is utilized to excite the sample using a spot size of $\approx 1 \ \mu\text{m}^2$. The spectrum is taken between the Raman shifts of 300 and 900 cm⁻¹.

Lithium Insertion Behaviour at Different pH



Figure S1: Li:Mn ratio measure by ICP-AES (red squares) and calculated from amount of charge passed (black squares) for nanowires held at 0 V vs. Ag/AgCl for 15 minutes. (Error bars represent 95% confidence intervals)

Manganese Mass at Negative Holding Potentials



Figure S2: Mass of manganese ions from ICP-AES results of manganese oxide nanowires held at the different potentials indicated on the x-axis for 15 minutes (Error bars represent 95% confidence intervals).

TEM Image at Full Lithiation



Figure S3: TEM image of a manganese oxide nanowire after charging at -1.0 V vs. Ag/AgCl for 15 minutes.





Figure S4: a. Galvannostatic charge/discharge curves for MnO_2 nanowires cycled between -1.0 and 1.0 V vs. Ag/AgCl at different charge densities in 0.1 M LiClO₄ acetonitrile (inset is same data as (a) plotted with time as the abscissa). b. Power capability of MnO_2 nanowires charged between -1.0 and 1.0 V (red squares) and 0 and 1.0 V (black squares) ('Calculated Li:Mn ratio' is calculated from the charge passed during the charging of the MnO_2 nanowires)