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Introduction

Portable electric energy storage issues associated with devices such as consumer electronics and electric vehicles, along with stationary electric energy storage concerns associated with renewable energy generation and the grid, continue to stimulate research in electric energy storage, including batteries.^{1,2} Thus, rechargeable lithium ion batteries (LIBs) occupy a prominent consumer presence due to their high cell potential and gravimetric energy density.^{2,3} However, long electrode cycle

Effective recycling of manganese oxide cathodes for lithium based batteries[†]

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While rechargeable lithium ion batteries (LIBs) occupy a prominent consumer presence due to their high cell potential and gravimetric energy density, there are limited opportunities for electrode recycling. Currently used or proposed cathode recycling processes are multistep procedures which involve sequences of mechanical, thermal, and chemical leaching, where only the base material is recovered and significant processing is required to generate a recycled electrode structure. Another significant issue facing lithium based batteries is capacity fade due to structural degradation of the electroactive material upon extending cycling. Herein, inspired by heterogeneous catalyst thermal regeneration strategies, we present a new facile cathode recycling process, where previously used cathodes are removed from a cell, heat treated, and then inserted into a new cell restoring the delivered capacity and cycle life. An environmentally sustainable manganese based material is employed, where binder-free self-supporting (BFSS) electrodes are prepared using a fibrous, high aspect ratio manganese oxide active material. After 200 discharge-charge cycles, the recycled BFSS electrodes display restored crystallinity and oxidation state of the manganese centers with the resulting electrochemistry (capacity and coulombic efficiency) reminiscent of freshly prepared BFSS cathodes. Notably, the BFSS electrode structure is robust with no degradation during the cell disassembly, electrode recovery, washing, and heat treatment steps; thus no postprocessing is required for the recycled electrode. This work shows for the first time that a thermal regeneration method previously employed in catalyst systems can fully restore battery electrochemical performance, demonstrating a novel electrode recycling process which could open up new possibilities for energy storage devices with extended electrode lifecycles.

lifetimes of LIBs remain a challenge. While a number of factors can contribute to limited LIB usable cycle lifetimes, cathode degradation is a significant factor.^{4–6} Thus, a variety of LIB cathode materials have been studied, including oxides of a variety of first row transition metals (*i.e.* Mn, Fe, V, Co, and Ni).^{7–9} Under extended lithiation/delithiation cycling, issues including structural strain, amorphization, and irreversible phase changes typically occur at the LIB cathode, resulting in an irreversible capacity loss.^{3,6,10–12} Thus environmental concerns, such as disposal and recycling issues, and economic concerns remain.^{1–3,5,13,14}

Currently used or proposed cathode recycling processes are multistep procedures which involve sequences of mechanical, thermal, and chemical leaching steps.^{13–16} During the mechanical recycling processes, the used cathodes are mechanically crushed and sieved multiple times and the components of the cathode are separated magnetically, gravimetrically (by density), and/or by size (sieving).^{13–15,17} However, separation is not always efficient; therefore further chemical leaching processes are frequently required for total recovery.^{15,18,19} Acid

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digestion is the most common chemical leaching process, and uses highly corrosive concentrated acids or bases.^{16,20} In addition, chemical leaching also requires a neutralizing chemical treatment to recover digested metals.^{13,20} A significant advance in this field was described recently whereby cathode powders from spent LiFePO₄ batteries could be recycled for the first time, using a heat-treatment process.²¹ However, the recycled electroactive material required significant reprocessing to generate a new cathode structure.

Herein we report a new cathode recycling process, inspired by heterogeneous catalyst thermal regeneration strategies. Binder-free self-supporting (BFSS) electrodes based on potassium containing cryptomelane-type manganese dioxide $(\alpha$ -MnO₂ structured KMnO₂) nanowires and multiwalled carbon nanotubes (MWNT) were developed and utilized for this approach. Notably, conventional composite coatings (typically a mixture of redox-active materials in combination with an electrically conductive material and a binder) deposited on metal current collectors are not suitable for the regeneration due to insufficient thermal stability of the binder or the metal current collector. However, the possibility of achieving mass savings and an increased energy density via the removal of the inert binder and the current collector is an added benefit of this electrode fabrication strategy. α-MnO₂, also referred to as OMS-2, is a polymorph of manganese dioxide formed by corner and edge sharing $[MnO_6]$ units forming intergrowth 2×2 $(4.6 \text{ \AA} \times 4.6 \text{ \AA})$ tunnels.²² In these materials, manganese is mixed valence (+3/+4) and the potassium cation (1+) is located in the tunnels to balance the overall charge.^{22,23} OMS-2 $(\alpha$ -MnO₂) has been previously used as a redox catalyst for selective or total oxidation of organic compounds.²³⁻³⁰ As a heterogeneous catalyst, the activity of OMS-2 decreases due to the depletion of labile surface oxygens, surface adsorbed species blocking the active sites, and/or reduction of manganese.^{25,28,30-34} OMS-2 catalysts can be regenerated by washing and/or heating under oxidative atmospheres such as air.^{25,30-34} Upon regeneration, the oxidation state of manganese is restored and the surface of the catalyst is repaired.^{25,28,30,32} Manganese oxides, when used as a cathode material in a battery electrode, experience a similar irreversible manganese reduction ($Mn^{4+} \rightarrow Mn^{3+} \rightarrow Mn^{2+}$), due to amorphization, crystal structure changes, and cathode dissolution (analogue of catalyst leaching).^{9,12,29,35-38} Our hypothesis was that it should be possible to restore the electrochemical activity of cycled (OMS-2/MWNT) BFSS cathodes by applying a thermal regeneration process inspired conceptually by a process developed for heterogeneous catalysts. This proof of concept study using OMS-2 as the electroactive cathode material introduces a new green chemistry recycling strategy which could be applied to other higher energy density electroactive materials in the future.

Results

The OMS-2 nanowires used for this study were prepared by a hydrothermal method to form long nanowires (>10 $\mu m)$



Fig. 1 Schematic representation of the cathode regeneration process: a coin-cell assembled with as-made binder free self-supporting cathode (BFSSC), 17 wt% MWNT + 83 wt% OMS-2 nanofiber. The used battery was disassembled and BFFSC was removed. BFSSC was regenerated by rinsing with DMC (dimethyl carbonate) first and then heating under air for 2 h at 300 °C. A new battery was assembled with the regenerated BFSSC. The same BFSSC can be regenerated and used multiple times without a notable performance loss.

grouped in bundles, Fig. S1.† The chemical formula of K_{0.84}Mn₈O₁₆·0.25H₂O was determined by XRD (for the structure, Fig. S2[†]), ICP-OES (potassium content), and TGA (water content, Fig. S3a[†]). OMS-2 nanofibers and MWNT were used to produce a thin, flat composite material resembling paper, where the OMS-2/MWNT ratio was 5/1 by weight. The dried "paper" composites were used directly as (OMS-2/MWNT) BFSS electrodes. The (OMS-2/MWNT) BFSS electrodes used for the regeneration studies have an average mass of 12 mg, a diameter of 1.27 cm, a thickness of 0.17 mm, and a BET surface area of 65 m² g⁻¹. Fig. 1 contains a diagram of our (OMS-2/MWNT) BFSS electrode regeneration process. After removal from the electrochemical cell, the intact, cycled (OMS-2/MWNT) BFSS electrodes were first rinsed with dimethyl carbonate (DMC) and then placed in an oven and heated under air (300 °C) for 2 h.

The (OMS-2/MWNT) BFSS electrode based cells using lithium metal anodes were galvanostatically cycled for 250 cycles, Fig. 2a. Under these conditions, the capacity of the (OMS-2/MWNT) BFSS cathode (control cell) was 112 mA h g⁻¹ for the first cycle and the capacity degraded to 13 mA h g⁻¹ at the end of 250 cycles. The initial capacity loss for the first 10 cycles was greater with more gradual capacity loss in subsequent cycles.

The capacity loss of OMS-2 (α -MnO₂) has been attributed to the structural degradation of manganese dioxide caused by Jahn–Teller distortion of reduced manganese species.^{12,39,40} Upon lithiation (discharge), Mn⁴⁺ species are reduced to Mn³⁺, with a concomitant amorphization of the oxide structure.^{11,29,37,41-44} Accordingly, the electrochemical oxidation of Mn³⁺ is not fully reversible, resulting in a loss of delivered capacity.

To our knowledge, this study is the first to demonstrate a successful battery electrode recovery and regeneration. In our electrode regeneration process, the electrode was first removed



Fig. 2 (a) Galvanostatic cycling performance and (b) coulombic efficiencies of the binder free self-supporting cathode (BFSSC) regenerated four times after every 50 cycles by rinsing with DMC first and then heating under air for 2 h at 300 °C; the control was cycled for 250 cycles. (c) Initial galvanostatic charge/discharge profiles of regenerated BFSSC after the regeneration steps. Cycle numbers are 1, 51 (after the 1st regeneration), 101 (after the 2nd regeneration), 151 (after the 3rd regeneration), and 201 (after the 4th regeneration). The current density was 50 mA g⁻¹ (2.0 and 3.9 V vs. Li/Li⁺).

intact from a battery which had undergone 50 cycles, and then regenerated by a simple thermal treatment under air and finally re-deployed in a new battery, Fig. 1. The electrochemical performance of the (OMS-2/MWNT) BFSS cathode recovered after regeneration is depicted in Fig. 2a. The regenerated (OMS-2/MWNT) BFSS cathode was treated after every 50 cycles while another (OMS-2/MWNT) BFSS cathode cycled for 250 cycles with no treatment was used as a control experiment. The initial capacity for both cell types was around 115 mA h g^{-1} . After the first 50 cycles, the capacity degraded to 43 mA h g⁻¹. After regeneration, the capacity of the cell was restored to 101 mA h g⁻¹. The process was repeated multiple (four) times with recovery of performance each time. A regeneration temperature of 300 °C was chosen in these studies considering the fact that thermal decomposition of MWCNT occurs at temperatures above 400 °C (Fig. S3b[†]). In addition, previous temperature programmed oxidation (TPO) studies on the used OMS-2 catalysts suggest that OMS-2 is completely oxidized at ~300 °C.³³

The delivered capacities were almost totally restored after each regeneration step. The initial capacity after each regeneration was higher than 95 mA h g⁻¹, suggesting an almost full recovery of the cathode performance each time. At the end of 250 cycles, the regenerated (OMS-2/MWNT) BFSS cathode delivered 60 mA h g⁻¹ capacity, which is almost five (5) times that of the (OMS-2/MWNT) BFSS cathode control cell. The effect of the regeneration on the coulombic efficiency was also encouraging, Fig. 2b. After the regeneration steps, except for the initial few cycles, the efficiencies remained above 95%. The initial discharge/charge voltage profiles after the regeneration steps are shown, are similar, and do not indicate a change in the lithiation mechanism, Fig. 2c. The discharge profiles of regenerated (OMS-2/MWNT) BFSS cathodes showed characteristics consistent with the as-prepared samples and are consistent with prior reports of voltage profiles for conventionally constructed OMS-2 (α -MnO₂) cathodes.^{35,36,44} In order to evaluate the importance of heat treatment on the electrochemistry of the regenerated cathode, another control experiment was performed by only rinsing the cycled (OMS-2/MWNT) BFSS cathodes and drying in a vacuum oven at room temperature. Fig. S4[†] shows the galvanostatic cyclic performance of regenerated (OMS-2/MWNT) BFSS electrodes without heat treatment where very similar results are observed.

As noted above, consecutive galvanostatic charge/discharge caused amorphization and reduction of the average oxidation state (AOS) of manganese. The effects of battery cycling and cathode regeneration on the crystallinity and average oxidation state (AOS) of BFSS cathode materials were determined using XRD (Fig. 3), XPS (Fig. 4 and Table 1) and high-resolution scanning transmission electron microscopy (STEM, see Fig. 5). The as-made (OMS-2/MWNT) BFSS cathodes, (OMS-2/MWNT) BFSS cathodes after 100 charge/discharge cycles, (OMS-2/MWNT) BFSS cathodes after 300 charge/discharge cycles, and regenerated (OMS-2/MWNT) BFSS cathodes after 100 charge/discharge cycles, discharge cycles were compared. Upon galvanostatic cycling of



Fig. 3 Effect of battery cycling and regeneration on the binder free self-supporting cathode (BFSSC). (a) X-ray Diffraction (XRD) patterns of as-made BFSSC and BFSSCs galvanostatically cycled for 100 and 300 times with a 50 mA g⁻¹ rate. (b) Scherrer crystallite sizes of the (200) and (310) planes of as-made, 100 times and 300 times cycled BFSSCs, and regenerated BFSSC after 100 cycles. (c) XRD patterns of as-made and regenerated BFSSCs. (d) Digital image of as-made BFSSC material along with the average weight (12.1 mg), thickness (0.17 mm), and BET surface area (65.2 m² g⁻¹). In BFSSC, the OMS-2/MWCNT weight ratio is 5/1, corresponding to 83 wt% of OMS-2.



Fig. 4 Structural changes of manganese and oxygen during the cathode regeneration. X-ray photoelectron spectra (XPS) of as-made BFSSC, BFSSCs galvanostatically cycled for 100 (BFSSC@100th cycle) and 300 (BFSSC@300th cycle) times with a 50 mA g⁻¹ rate, and regenerated BFSSC after 100 cycles. (a) Mn 3s spectral region: with increasing cycle number the Mn 3s peak separation (indicated by \leftrightarrow) increases gradually and decreases after the regeneration step. (b) O 1s spectral regions. The O 1s spectral region was deconvoluted into three chemical states: lattice (O_{lat}), surface (O_{surf}), and adsorbed (physisorbed species, *i.e.* water) (O_{ads}) oxygen species.

(OMS-2/MWNT) BFSS cathodes, the X-ray diffraction line intensities showed significant decreases and broadening (Fig. 3a). However, all the diffraction lines could be still indexed to the pure cryptomelane phase of manganese dioxide ($K_xMn_8O_{16}$, JSPDS: 00-029-10). Common impurity phases such as Mn_2O_3 , Mn_3O_4 , Li Mn_2O_4 and MnOOH were not detected. Scherrer crystallite sizes of the two most intense (310) and (200) diffraction lines were calculated, Fig. 3b. Upon cycling, the peaks in the XRD patterns broadened and crystallite sizes decreased significantly (indicated by a black arrow in Fig. 3b), assuming that the changes were dominated by crystallite size reduction. Thus, the crystallite size along the (310) direction decreased from 18 to 15 nm after 100 cycles and to 13 nm after 300 cycles. The (200) crystallite size also showed a similar trend and gradually decreased from 17 to 11 nm after 300 cycles. The data clearly suggest amorphization upon charge/discharge cycles consistent with previous findings.^{39,40} XRD data of the as-made and of the regenerated BFSS cathodes after 100 cycles are shown in Fig. 3c where after regeneration, the diffraction patterns almost look identical. Calculation of the crystallite size confirmed that the crystallite size increased upon regeneration (Fig. 3b). The (310) crystallite size increased from 15 to 17 nm and the (200) crystallite size increased from 15 to 17 nm after regeneration. Thus, the as-prepared BFSS cathode had a similar crystallite size to the regenerated cycled BFSS cathode. The (OMS-2/MWNT) BFSS electrodes are structurally robust (Fig. 3d), showed no mechanical degradation after cycling, and could easily be handled, both before and after regeneration (Fig. S5[†]).

The average oxidation state (AOS) of manganese was determined by the splitting of Mn 3s peaks in XPS, Fig. 4a. Mn 3s peak splitting ($\Delta E_{Mn 3s}$) originates from the coupling between 3s hole and 3d electrons and the magnitude of the splitting linearly correlates with the AOS of manganese, 45 AOS = 8.956 – $1.126 \times \Delta E_{Mn 3s}$.⁴⁵⁻⁴⁷ Table 1 summarizes Mn 3s binding energies (BEs), $\Delta E_{Mn 3s}$ and AOS. The AOS of the as-made BFSSC was 3.83; however, upon cycling the AOS gradually decreased to 3.20 after 100 cycles and to 2.43 after 300 cycles. Notably, the regeneration treatment restored the oxidation state to 3.79. To gain a better understanding of the effect of battery cycling and regeneration on the surface structure of manganese, O 1s spectra were also recorded (Fig. 4b). O 1s peaks were deconvoluted to three different chemical states: (1) lattice oxygen (O_{lat}) , (2) surface hydroxyl groups and surface adsorbed cations (Osurf), and (3) surface adsorbed species, *i.e.* water and polycarbonates (O_{ads}).⁴⁸⁻⁵⁰ Relative peak area comparison suggested that 78.1% oxygen in the as-made (OMS-2/MWNT) BFSS cathodes is in the form of lattice oxygen (Olat) (Table 1). Upon cycling, the amount of lattice oxygen decreased gradually; to

\mathbf{T}	Table 1	XPS summary	v of as-made	cvcled	, and red	enerated	binder free	e self-sui	oportina	cathodes	(BFSSG	C)
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	Mn 3s (eV))		O 1s			
Sample	$\overline{\mathrm{BE}_1}^a$	${\operatorname{BE}_2}^a$	ΔE^{b}	State ^c	BE (eV)	Area (%)	Average Mn oxidation state ^d
As-made BFSSC	88.54	83.99	4.55	O _{lat}	529.2	78.1	3.83
				O _{surf}	530.7	12.0	
				O _{ads}	532.0	9.9	
BFSSC@100 th cycle	88.95	83.83	5.12	O _{lat}	529.1	45.5	3.20
_ •				O _{surf}	530.5	51.9	
				O _{ads}	533.7	2.6	
BFSSC@300 th cycle	89.14	83.35	5.79	O _{lat}	529.3	12.4	2.43
-				O _{surf}	531.0	67.3	
				O _{ads}	533.7	20.3	
Regenerated BFSSC ^e	88.49	83.91	4.58	O _{lat}	529.3	67.9	3.79
0				O _{surf}	530.8	22.5	
				Oade	532.4	9.6	

^{*a*} Binding energies of two chemical states were obtained for Mn 3s photoelectrons. ^{*b*} $\Delta E = BE_1 - BE_2$ of Mn 3s photoelectrons. ^{*c*} Three different chemical states of O as indicated were obtained from the O 1s spectral region. ^{*d*} Average oxidation states (AOS) were calculated from the ΔE of Mn 3s peaks (AOS = 8.956 - 1.126 × $\Delta E_{(3s)}$). ^{*e*} The cathode was regenerated after 100 charge/discharge cycles.



Fig. 5 High-resolution STEM images showing crystallinity and amorphization of the as-made, 100 cycled, 300 cycled and regenerated binder free self-supporting cathode (BFSSC). (a) The as-made BFSSC sample viewed along the [012] direction, revealing high crystallinity throughout the entire nanorod with a clean crystalline surface (scale bar 5 nm). The inset is a magnified area from the boxed region from the edge embedded with the structural model (scale bar 1 nm). (b) The BFSSC sample cycled for 100 times viewed along the [015] zone axis (scale bar 5 nm). Although overall the nanorod remains crystalline, the fuzzy contrast and spackle intensity suggest significant amorphization on the sample. The amorphous patches appearing at the edge of the image (see the inset) indicate that they cover the entire surface of the nanorod. Lattice distortion related defects were also observed. (c) The BFSSC sample cycled for 300 times (scale bar 5 nm). Very thick amorphous layers on the surface make the atomic structure in the interior of the nanorod barely visible. (d) The regenerated BFSSC sample after 100 cycles viewed along the [1–21] direction (scale bar 5 nm). The amorphous patches on the surface (see the enlarge image in the inset from the same boxed area at the edge) have clearly transformed into a single crystal, consistent with the X-ray and electrochemistry data.

45.5% after 100 cycles and to 12.4% after 300 cycles. Nevertheless, the amounts of surface oxygen species (O_{surf}) increased from 12% to 51.9% at the end of 100 cycles and to 67.3% at the end of 300 cycles. The decrease in the relative amounts of lattice oxygen suggests the formation of a poorly condensed oxide structure, also evidenced by the amorphization of BFSS cathodes after repeated discharge/charge cycling (see Fig. 3). The relative amount of lattice oxygen (Olat) increased from 45.5 to 67.9% after cathode regeneration. It appears that high temperature regeneration (at 300 °C) under an oxidative atmosphere (air) promoted reoxidation and condensation of the manganese oxide structure in the cycled BFSS cathodes. The oxygen peaks for adsorbed species (O_{ads}) shifted to slightly higher binding energies (532.0 to 533.7 eV) after battery cycling, suggesting an adsorbed specie other than surface adsorbed water, see Table 1.48,49,51

To compare the crystal structure and morphology of the BFSS cathodes at different charge/discharge cycles (0, 100, and 300) and after the regeneration process, high-resolution electron microscopy was used. Here, we present the HAADF (high-angle annular-dark-field) STEM (scanning transmission electron microscopy) images, taking advantage of the HAADF imaging mode whose contrast is very sensitive to crystalline quality, typical examples in Fig. 5. In the as-made BFSS electrodes, the nanorods exhibit high crystallinity with a clean surface, Fig. 5a. After 100 cycles, a significant morphological change was observed, Fig. 5b. Amorphous patches, 2-4 nm in size, form on the surfaces, seen as speckle contrast on the top and at the edge of the nanorod in Fig. 5b. We also noticed that after repeated charge/discharge cycles, the size of the crystalline nanorods reduces (Fig. S7[†]). Structural defects (mosaic lattice distortion, marked by the circle) were also observed, indicating the consecutive galvanostatic charge/discharge caused structure degradation of the manganese dioxide. The defects induce local strain, which also contributes to the peak broadening observed in XRD. For a BFSS cathode after 300 cycles, Fig. 5c, we observe the formation of considerably thick and large amorphous patches that cover the entire surface although the interior of the nanorods remains crystallized. However, after the regeneration process, the surface amorphous patches on the 100 cycled BFSS cathode sample almost completely disappeared and transformed into crystalline material, while the patch morphology persisted on the surface, Fig. 5d. The observed improvement in capacities of the regenerated samples indicates that the recrystallization is the key for the restoration of the oxidation state of the cathode.

Discussion

Upon extended galvanostatic charge/discharge cycling, the electrochemical performance of (OMS-2/MWNT) BFSS electrodes decreased from 115 to 13 mA h g⁻¹ after 250 cycles. The performance loss was attributed to the structural degradation (reduction and amorphization) of OMS-2 ($K_{0.84}$ Mn₈O₁₆· 0.25H₂O) as evidenced by XRD (Fig. 3a), XPS (Fig. 4), and high resolution electron microscopy (Fig. 5) analyses. Here, a simple regeneration process was applied by rinsing the cathode and heating it under air to restore both the manganese oxidation state and crystallinity of the OMS-2 cathode (see Fig. 1). Regenerated BFSS electrodes had very similar crystallite sizes (18 *vs.* 17 nm), AOS (3.83 *vs.* 3.79), and galvanostatic cycling performance to the as-made BFSS electrodes (Fig. 2). The BFSS electrode was regenerated four times and performance was restored each time.

The role of OMS-2 (α -MnO₂) as a heterogeneous catalyst in redox reactions is quite different from its role as a cathode. As a catalyst, substrates are adsorbed on the catalyst surface, selectively or totally oxidized by labile surface oxygens, and desorbed from the surface (Mars-van Krevelen mechanism).²⁸ The reduced catalyst surface is reactivated and oxygen vacancies are filled via introduction of an additional oxidizing agent (i.e. oxygen from air) to make the catalyst surface available for further reactions. It has been previously reported that adsorbed carboxyl groups on manganese oxide surfaces can reduce the manganese during heat treatment under air,⁵² thus surface conditions and cleanliness prior to the reactivation step are important in catalysis. On the other hand in batteries, OMS-2 reversibly hosts Li^+ (MnO₂ + Li^+ + $e^- \rightleftharpoons \text{Li}_x \text{MnO}_2$)^{9,35} and can experience structural changes causing performance losses, including amorphization of the oxide structure, reduction of manganese and formation of surface adsorbed species upon extended discharge/charge cycling. Here we show that the AOS, crystallinity, and surface structure of OMS-2 can be restored by BFSS electrode regeneration.^{25,30-34} Therefore, our hypothesis that the electrochemical performance of manganese oxide based cathodes could be restored by a regeneration process was experimentally affirmed, and to the best of our knowledge, this is the first study to propose and demonstrate cathode regeneration for batteries. Broader implications of this work could lead to recycling of both anodes and cathodes by similar strategies to restore electrode performance and significantly extend battery lifetimes.

Conclusion

In summary, binder free self-supporting (BFSS) electrodes were made based on a low cost cathode material (manganese oxide) OMS-2 (α -MnO₂) nanowire active material. The electrochemical function of these electrodes could be restored multiple times by a simple thermal regeneration process. Each time the recycling process restored the average oxidation state of the manganese centers, crystallinity, and the electrochemical performance. This work demonstrates for the first time that a thermal regeneration method previously employed in catalyst systems is applicable to battery electrodes providing a path to effectively recycle not only active material, but entire electrode structures. While the particulars of the heat treatment methodology described here were developed specifically for the cryptomelane type manganese dioxide (OMS-2) BFSS electrodes used in this study, this electrode recovery, heat treatment, and recycling strategy could be implemented for other electrode materials with nanowire morphology, where a similar oxidative treatment should be appropriate for other cathode materials and a reductive treatment may be useful for anodes. In a broader sense, the development of electrode recycling processes could open up new possibilities for energy storage devices with extended electrode lifecycles.

Experimental

Materials synthesis

A cryptomelane type manganese dioxide nanowire, an octahedral molecular sieve (OMS-2), was synthesized by a modified version of a previously reported hydrothermal method.⁵³ In a typical synthesis procedure, manganese sulfate monohydrate ($Mn(SO_4) \cdot H_2O$), potassium sulfate (K_2SO_4), potassium persulfate ($K_2S_2O_8$), and DDI water were mixed with a ratio of reactants of 1:2:1:555.6. The reagents were heated in a stainless steel autoclave at 200 °C.

Preparation and regeneration of binder free self-supporting (BFSS) electrodes

The as-made OMS-2 material was dispersed in water, acetone, and then 1-methyl-2-pyrrolidone (NMP). This suspension of OMS-2 nanowires in NMP was added to a multiwalled carbon nanotube (MWNT) suspension at a OMS-2/MWCNT weight ratio of 5:1. After sonication, the suspension was filtered, rinsed and dried under vacuum. The BFSS electrodes were pressed to yield circular pieces with 1.27 cm diameter. For regeneration, the cycled cells were opened; the BFSS electrode was removed, rinsed with dimethyl carbonate, dried in a vacuum oven, heated to 300 °C at a 2 °C min⁻¹ rate for 2 h in a box oven under air (ambient conditions) and used without further treatment.

Materials characterization

X-ray diffraction (XRD) patterns of BFSSCs were collected using a Rigaku SmartLab X-ray powder diffractometer with Cu K α radiation. N₂ sorption (adsorption–desorption) measurements were performed on a Quantachrome Nova 4200e instrument and a multipoint BET (Brunauer, Emmett, and Teller) method was used for calculating the surface area. Thermogravimetric analysis (TGA) was performed with a TA Instruments SDT

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Q600 instrument under 10 cc min⁻¹ air flow and from 25-900 °C. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was done using a Thermo Scientific iCAP 6000 series spectrometer. Scanning electron microscopy (SEM) images and energy dispersive spectra (EDS) of the OMS-2 samples were collected using a JEOL JSM-6010PLUS instrument with an accelerating voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) experiments were carried out in a UHV chamber equipped with a SPECS Phoibos 100 MCD analyzer and a non-monochromatized Al-K α X-ray source ($h\nu$ = 1486.6 eV) operating with an accelerating voltage of 10 kV and 30 mA current. The chamber typically has a base pressure of 2×10^{-10} Torr. The samples were placed onto a conductive copper tape and mounted on a sample holder. Charging effects were corrected by adjusting the binding energy of the C (1s) peak at 284.8 eV.⁴⁹ High-resolution TEM/STEM imaging was performed using the double aberration-corrected JEOL-ARM200CF microscope with a cold-field emission gun and operated at 200 kV. The microscope is equipped with JEOL and Gatan HAADF detectors for incoherent HAADF (Z-contrast) imaging.

Electrochemical characterization

Stainless steel experimental coin cells with lithium metal anodes were fabricated under an argon atmosphere glove box. OMS-2/MWNT BFSS cathodes, lithium metal anodes, and the electrolyte consisting of 1 M LiPF₆ in ethylene carbonate-dimethylcarbonate (30:70 wt ratio) were used. The cells were cycled under a 50 mA g⁻¹ rate. At the end of 50 cycles the BFSS electrodes were regenerated and new coin cells were assembled. For the control experiment, a BFSS electrode containing cell was cycled 300 times.

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