Synthesis of High Surface Area $\alpha$-K$_y$MnO$_2$ Nanoneedles Using Extract of Broccoli as Bioactive Reducing Agent and Application in Lithium Battery

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Abstract: With the aim to reduce the entire cost of lithium-ion batteries and to diminish the environmental impact, the extract of broccoli is used as a strong benign reducing agent for potassium permanganate to synthesize $\alpha$-K$_y$MnO$_2$ cathode material with pure nanostructured phase. Material purity is confirmed by X-ray powder diffraction and thermogravimetric analyses. Images of transmission electron microscopy show samples with a spider-net shape consisting of very fine interconnected nanoneedles. The nanostructure is characterized by crystallite of 4.4 nm in diameter and large surface area of 160.7 m$^2$ g$^{-1}$. The material delivers an initial capacity of 211 mAh g$^{-1}$ with high Coulombic efficiency of 99% and 82% capacity retention after 100 cycles. Thus, $\alpha$-K$_y$MnO$_2$ synthesized via a green process exhibits very promising electrochemical performance in terms of initial capacity, cycling stability and rate capability.

Keywords: $\alpha$-K$_y$MnO$_2$; nanoneedles; lithium-ion batteries; green synthesis; cathode

1. Introduction

Lithium-ion batteries (LiBs) have been widely used to power many systems (e.g., portable electronics, tools, hybrid and electric vehicles, etc.) [1–3]. However, to increase the gravimetric energy density, it is necessary to find optimized, safe and suitable electrode materials, which are the limiting elements of LiBs [4,5].

Manganese dioxide (MDO) is an abundant, rather cheap and green material, which is not only used in primary lithium batteries [6], but also developed as advanced electrode material for Li-ion, Li-sulfur or Li-air secondary batteries [7–13]. It can deliver a theoretical capacity of ~320 mAh g$^{-1}$ based on the transfer of one electron per formula in the potential range of 1.5–4.0 V (vs. Li$^+/Li$). In addition to applications in batteries, MnO$_2$ has also been used as a component in composite electrodes for electrochemical supercapacitors [14]. It crystallizes in various polymorphic forms, e.g., $\alpha$-, $\beta$-, $\gamma$-, $\lambda$- and $\delta$-MnO$_2$, etc., which differ from each other by the different assembly of octahedral MnO$_6$ units. Thus, the electrochemical performance of MnO$_2$ strongly depend on the number of sites available for Li-ion insertion in its tunnel framework. According to different conditions of...
reaction or synthesis methods, MnO$_2$ can be obtained with various morphologies (e.g., nanowires (NWs), nanoneedles (NNs), nanofibers (NFs), nanofoils (NFs), nanosheets (NSs), nanorods (NRs), etc.) that promote suitable electrode material for LiBs [10]. According to intensive investigations on nanostructured materials, the needle-shaped specimen is proved to be a good choice in order to enhance the electrochemical performance of MnO$_2$ [15]. The nanoscale and nano-fiber-type morphology can provide more active sites for Faradaic reaction and, hence, reduce the diffusion time of lithium ions in the core of particles due to the one-dimensional transport pathway and the large surface-to-volume ratio [16].

Among different MnO$_2$ polymorphs, the tetragonal α-phase has attracted special attention because its large 2 × 2 tunnels are favorable for the transportation and accommodation of foreign ions [17,18], such as K$^+$ in the cryptomelane-type K$_x$Mn$_8$O$_{16}$ compounds [19]. Zhang et al. reported that K$_{0.25}$Mn$_2$O$_4$ nanofibers exhibit excellent lithium insertion properties with high charge capacities and good rate capability [20].

The preparation of α-MnO$_2$ nanostructured particles has been realized by different techniques, including co-precipitation [16], comproportionation [21], hydrothermal [22], sonochemical reduction [23], micro-emulsion route [24], simple redox reaction [25] and reflux method [26]. Green synthesis is also one of these approaches using extracts of plants as reducing agents taking into account the presence of flavonoids and polyphenols [27–29]. Phenolic compounds are characterized to have at least one aromatic ring attached to one or more hydroxyl groups, with various arrangements of their carbon atoms. The reducing or antioxidant ability of flavonoids and phenolic acids is closely related to the number and position of hydroxyl groups in the molecule. The higher the number of hydroxyl groups, the higher the antioxidant activity [30]. Previously, we reported successful preparations of nanostructured MnO$_2$ via biological reducing agents such as extract of green and black tea [27], citrus peel [31], and extract of orange peel [25]. Broccoli is a kind of vegetable similar to cauliflower and cabbage, all of them are rich in natural antioxidants, antimicrobial and anticancer activities [32]. Such vegetables have a high number of phenolic components and are appreciable sources of polyphenols, especially flavonoids [33]. Figure 1 shows a schematic representation of the chemical composition of broccoli extract including the antioxidant species (i.e., α-lipoic acid, sulforaphane and coenzyme Q10) [32,34]. These flavonoids and phenolic acids are present in leaves, flowering tissues and other parts of the broccoli plant.

![Figure 1](image_url)

**Figure 1.** Schematic representation of the chemical composition of broccoli extract. Chemical structure of (a) sulforaphane, (b) vitamin coenzyme Q10 and (c) α-lipoic acid.

The aim of this work is to prepare α-K$_x$MnO$_2$ nanoneedles with a low concentration of potassium ions using a two-step green synthesis approach with the extract of broccoli plant as reducing agent, and to investigate the electrochemical performance of the as-prepared sample. The structure and morphology of the prepared sample are investigated by X-ray diffraction (XRD), thermal gravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) specific surface area method, and transmission electron microscopy (TEM). Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) experiments are carried out in lithium-metal cells with α-K$_x$MnO$_2$ as the positive electrode. Finally, the rate capability and cyclability of α-K$_x$MnO$_2$ NNs are further investigated.
2. Materials and Methods

All chemicals were analytical grade and used without further purifying. The redox reaction between KMnO₄ (oxidizing agent) and the extract of broccoli (reducing agent) was directly employed to prepare KₓMnO₂ nanowires without templates or surfactants, thus the synthesis can be considered as a green approach. A concentrated extract of broccoli sprouts was obtained through fresh seasonal vegetables cleaned in distilled water followed by 10 min boiling at 100 °C [35]. After filtration of the decoction, the bioactive compound (2 g) was added to 3 g of KMnO₄ (19 mmol) dissolved in 100 mL distilled water (DI) and acidified with 2 mL of 2.5 mol L⁻¹ H₂SO₄. The entire mixture was stirred vigorously for 1 h at room temperature. Then, a change in color from purple to black was observed as K MnO₄ was completely reduced by the broccoli extract and black precipitate was formed. The precipitate was isolated by filtration and washed several times by distilled water, then was dried overnight at 90 °C and further calcined at 300 °C for 5 h in air.

The crystal structure of the final product was determined by XRD using Philips X’Pert apparatus (Philips, Hambourg, Germany) equipped with a CuKα X-ray source (λ = 1.54056 Å) in the 2θ range of 10–80°. TGA measurements were carried out using a thermal gravimetric analyzer (Perkin Elmer, TGA 7 series, Baesweiler, Germany) in the temperature range of 50–1000 °C at a heating rate of 10 °C min⁻¹ in air. The morphology of the prepared sample was investigated by transmission electron microscopy (TEM, JEOL, JEM-2100, Electron microscope, Tokyo, Japan). The BET specific surface area was measured by nitrogen adsorption/desorption at 77 K in a relative pressure 𝑃/𝑃₀ = 0.0–1.0, with 𝑃 and 𝑃₀ being the equilibrium and saturation pressure, respectively, using a Quantachrome NOVA Automated Gas Sorption analyzer (Anton Paar GmbH, Blankenfelde-Mahlow, Germany). The pore size distribution and pore volume were estimated using the Barrett–Joyner–Halenda (BJH) method [36].

Electrodes for electrochemical testing were prepared by casting a slurry (N-methyl-2-pyrrolidone (NMP) used as the processing solvent) composed with 85 wt.% α-KₓMnO₂ active material, 10 wt.% conductive carbon C65 (TIMCAL), and 5 wt.% polyvinylidene fluoride (PVdF) onto an Al foil. The dried sheet was punched into Ø 12 mm discs, and the mass loading of active material was evaluated to be 1.2–1.3 mg cm⁻². These positive electrodes were assembled inside 2016 coin cells with Li metal foil as the counter electrode and 1 mol L⁻¹ LiPF₆ in ethylene carbonate:dimethyl carbonate (EC:DMC, 1:1 in vol.) as electrolyte. Cyclic voltammetry measurements were carried out at scan rate of 0.2 mV s⁻¹ using a coin-cell with a 2-electrode configuration, that implies cumulative electrochemical response of both electrodes. The cycling and rate performance were obtained by galvanostatically discharging and charging cells on a Maccor series 4000 battery tester (Maccor Inc., Tulsa, OK, USA) between 4.0 and 1.5 V at 25 °C under different current densities from 0.1 to 10 C rate (1 C = 320 mAh g⁻¹).

3. Results

3.1. Morphology, Structure and Composition

The structure, composition and morphology of the as-prepared KₓMnO₂ were investigated by XRD, TGA, BET and TEM measurements. Particular attention was paid to characterize the crystal-chemistry of KₓMnO₂ synthesized via the reduction of potassium permanganate, which always induces a residual fraction of K⁺ ions (VIIIK ionic radius of 1.51 Å) located in the 2 × 2 tunnels of the α-MnO₂ lattice, whose main functions are templating and stabilizing the tunneled network [37]. Although numerous works published in the literature neglect this aspect. Several articles considered the presence of potassium as the combined outcome of the preparation of cryptomelane or birnessite MnO₂ phases [27,38–40]. As a result, mixed +4 and +3 oxidation states of Mn cations could be induced in the α-MnO₂ (Mn₈O₁₆) lattice (i.e., KMn⁴⁺₂Mn¹⁺⁶O₁₆). Thus, the degree of insertion of K⁺ ions located in the crystal tunnels depends on the synthesis process as it will be discussed in infra.

SEM and TEM images of KₓMnO₂ are shown in Figure 2a–d. In the SEM picture (Figure 2a), micron-sized particles with average size ~500 nm have almost identical shape and distribution. The sample calcined at 300 °C for 5 h in air grows with the morphology of secondary particles (agglomerates)
composed of interconnected nanoneedles. Particles are constituted by a complex arrangement of very fine interconnected nanoneedles with diameters in the range of 5–20 nm and lengths of 100–300 nm. Thus, K\textsubscript{y}MnO\textsubscript{2} architecture is an assembly of nanoneedles interwoven into a mesoporous network as it will be characterized in infra. The HRTEM bright-field image of a selected well-crystallized nanoneedle (Figure 2d) displays uniform lattice fringes with an interplanar distance of 0.70 nm, which corresponds to the separation between the (110) crystal planes of the α-MnO\textsubscript{2} phase indicating the well-ordered tunnel structure along the b-axis. These images suggest that the shape and small size of nanoparticles can be attributed to the fast reduction process of KMnO\textsubscript{4} [16] and the acidification by 2.5 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4}. The dependence of chemical composition, the nanoparticle size and lattice structure with growing conditions (i.e., temperature and acidity) has been investigated in previous works [41–46]. For example, the cryptomelane phase is formed in an acidic solution, while the birnessite-type MnO\textsubscript{2} is synthesized in a basic solution. Portehault at al. obtained cryptomelane nanowires (15–40 nm in diameter) when the pH value of the solution has been controlled in the range of 0.9–1.25 [21]. It appears that up-scalable synthesis can be achieved using a facile method at low temperature with very cheap green chemistry. Villegas et al. showed that the reduction of KMnO\textsubscript{4} by H\textsubscript{2}O\textsubscript{2} under acidic condition produced NNs with width of a few tens of nanometers [45]. In contrast, Kumar et al. addressed the preparation of highly-dispersed α-MnO\textsubscript{2} NNs (20–30 nm in size) without K\textsuperscript{+} inclusion using a sonochemical hydrolysis of Mn(3)acetate with a solution close to neutral pH followed by mild drying [46].

**Figure 2.** (a) SEM images of cryptomelane-type K\textsubscript{y}MnO\textsubscript{2} nanoneedles, (b) TEM image showing the interconnected nanoneedles and (c,d) HRTEM images. The lattice fringes (image (c)) show an interplanar distance of 0.70 nm, which corresponds to the separation between the (110) crystal planes in the cryptomelane α-MnO\textsubscript{2} structure.

Figure 3a shows the XRD pattern of as-prepared K\textsubscript{y}MnO\textsubscript{2} NNs. The main characteristic peak appearing at 2\textdegree TH value of 37° is indexed to the (211) plane, while other diffraction peaks at 42.0°, 55.5° and 66.4° with low intensity in pattern are assigned to the (301), (600) and (002) planes, respectively, of the tetragonal α-MnO\textsubscript{2} phase (space group 14/m, JCPDS 44-0141) with no apparent impurities. No diffraction pattern attributable to other crystallographic MnO\textsubscript{2} is observed. The low intensity is due to the poor crystallinity and the peak broadening indicates the nanosized character of α-K\textsubscript{y}MnO\textsubscript{2} samples. The refined lattice parameters are \(a = 9.95(2)\) Å, \(c = 2.76(7)\) Å and \(V = 274.1\) Å\(^3\). A comparison with values of the α-MnO\textsubscript{2} crystal (JCPDS card 44-0141, \(a = 9.7845\) Å, \(c = 2.8630\) Å) confirms the lattice expansion along the a-axis direction, which may have originated by the presence of bigger six-coordinated Mn\textsuperscript{3+} ions (high-spin state, \(r_{\text{Mn}^{3+}} = 0.645\) Å) than Mn\textsuperscript{4+} (\(r_{\text{Mn}^{4+}} = 0.53\) Å). Meanwhile, the elementary unit volume matches well with values of the α-K\textsubscript{y}MnO\textsubscript{2} structure, in which a low concentration of K\textsuperscript{+} ions is inserted in the 2 × 2 tunnels (i.e., typically \(y < 4\) in α-K\textsubscript{y}Mn\textsubscript{8}O\textsubscript{16}) [43]. For
example, a slight bigger elementary volume of 279.6 Å³ was reported by Vicat et al. for K₁₃₃Mn₈O₁₆ [19]. Scherrer crystallite size calculated from the half-width at half-maximum of the (211) diffraction line at 2θ ≈ 37.6° is found to be 4.4 nm, showing the polycrystalline character of α-K₉MnO₄ NNS. The combination of XRD data and HRTEM image reveals that NNSs are composed of a few aggregated crystallites. This result is comparable with those obtained from α-K₉MnO₄ nanoneedles prepared by the mild synthetic method using the extract of tea as reducing agent, in which XRD patterns are dominated by the (211) Bragg line and the crystallite size is found to be ~4 nm [27].

Figure 3b shows the N₂ adsorption desorption isotherm and Barrett–Joyner–Halenda (BJH) pore-size distribution for as-prepared α-K₉MnO₄. It can be noticed that the isotherm curve displays an increase in the amount of adsorbed N₂ with increase of the P/P₀ value; the appearance of a hysteresis loop indicates the hierarchical mesoporous structure of α-K₉MnO₄ NNSs. At P/P₀ = 0.97, the volume of N₂ adsorbed is found to be 450 cm³ g⁻¹. The mesoporous nature of the as-prepared α-K₉MnO₄ is also illustrated by the graph in inset of Figure 3b, which was obtained according to BJH method. Suib et al. [47] have described the formation of mesoporosity by aggregation of MnO₂ nanoparticles (nanorods or nanoneedles) along the lateral faces. The mesopore-size distribution in the range 1–20 nm displays a single peak centered at 10.4 nm, with total pore volume of 0.950 cm³ g⁻¹. The α-K₉MnO₄ samples (powders) are composed of secondary particles (agglomerates), which are interconnected nanoneedles (primary particles) with diameters in the range of 5–20 nm and lengths of 100–300 nm. The mesopores (10 nm in size) correspond to the intraconnecting voids existing between randomly-packed nanoneedles [47].

The effects of the particle size and the surface area of the nanostructured MnO₂ materials were studied extensively (see, for example, [47–55]) because the mesoporous structure plays a significant role in enhancing the active sites at electrode surface and improves the electrochemical properties sequentially. Xia et al. stated that the mesopore size for MnO₂ decreases from 8 to 4 nm with the increase of the hydrothermal synthesis temperature [48]. Li et al. reported an average mesopore diameter of ~8 nm for mesoporous MnO₂ with a BET surface area of 226 m² g⁻¹ [49] The BET surface area value of 161 m² g⁻¹ is greater than values reported for MnO₂ prepared by different methods (e.g., microemulsion method (123 m² g⁻¹) [50], hydrothermal synthesis (150 m² g⁻¹) [51], silica templating combined with ion-exchange route (142 m² g⁻¹) [52], mild reaction [53] and exfoliation [49]).

Thus, the synthesis technique used in this work appears to be efficient in providing mesoporous pure α-phase K₉MnO₄ NNSs with relatively small particles. The K-birnessite-type MnO₂ hydrothermally synthesized at 160 °C for 30 min exhibits a narrow pore size distribution around 5.4 nm [54]. Regarding the HRTEM results, the pore size value describes cross-section of a single nano-needle. The value of 10 nm is in good agreement with the inner diameter measured by HRTEM. Similar results were reported for mesoporous α-MnO₂ nanorods (NRs) synthesized by reduction of KMnO₄ with a triblock polymer assisted by sonication (i.e., a pore volume of 1.0 cm³ g⁻¹ but smaller pore diameter of 13.5 nm) [23].
mesoporous MnO2 nanorods prepared by the solvent-free synthesis method show a unique pore-size distribution peak positioned at 16 nm [55].

The chemical composition of KxMnO2 NNs analyzed by inductively-coupled plasma (ICP) measurements shows 52.62 wt.% Mn and 1.45 wt.% K. This result confirms that the cryptomelane-type sample contains a small concentration of potassium. The formula can be calculated as α-K0.03MnO2, taking into account the error of measurements. The presence of K⁺ ions inside 2 × 2 tunnels is considered to be positive to stabilize the tetragonal structure and enhance the Li-diffusion kinetics [56].

This composition as well as the chemisorbed water were further determined by thermogravimetry (TG). The TG curve shown in Figure 4a displays three distinct weight losses. A first step of ~10% at ca. 120 °C (region I) is attributed to the loss of moisture from the sample surface. The second weight loss of ~20% in the range 200–400 °C (region II) is due to the removal of structural water. The third step (viewed as a fast drop) in the range of 480–520 °C (region III) is signed to the reduction of MnO2 to the non-conductive Mn1.98O3 (dense bixbyite structure) occurring with a release of oxygen (2MnO2→Mn1.98O3 + 1/2O2) via an exothermic reaction [57]. Several studies have shown that the onset temperature of the rapid weight loss in region III depends on the concentration of tunneled foreign ions (potassium or ammonium) in the cryptomelane K2Mn8O16 structure [39,58]. Generally, the MnO2→Mn1.98O3 transformation occurs in the temperature range of 480–670 °C, 480 °C being the decomposition temperature for a material without any large stabilizing cations and 670 °C being the transformation temperature of K2Mn8O16 to bixbyite [59]. The decomposition temperature of 504 °C was estimated from the differential (DTG) weight loss as shown in Figure 4b. Using different DTG behaviors of the literature, it was found that there is an almost linear relationship between the transition temperature and the content of K⁺ ions in α-KxMnO16. According to Figure 2 shown in [27], we can estimate a concentration of potassium (i.e., x = 0.035), which is close to the value obtained from ICP measurement. Thus, the amount of electrochemically inactive K⁺ ions (1.45 wt.%) is confirmed to be much smaller than that of Mn (52.82 wt.%), and does not obviously affect the specific capacity of the electrode.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** (a) TG curve of green synthesized KxMnO2 nanoneedles. (b) Differential weight dW/dT showing the decomposition temperature from α-KxMnO2 to Mn2O3.

3.2. Electrochemical Performance

The suitability of the α-KxMnO2 nanoneedles as a cathode material for lithium batteries was tested electrochemically by cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) experiments using 2016-type coin cells. All measurements were carried out at room temperature. Note that without reference electrode, the choice of cell voltage range should exclude that of the lithium electrode. Figure 5a shows the CV curves of α-KxMnO2 NNs recorded at scan rate of 0.1 mV s⁻¹ within the voltage range of 1.0–4.0 V. The redox peak is attributed to the Li insertion associated with the Mn⁴⁺/Mn³⁺ couple. The initial open circuit voltage (OCV) of the cell with α-KxMnO2 NNs electrode was 3.08 V. The broadening of CV peaks is attributed to the poor crystallinity of α-KxMnO2 electrode [27] rather than the nanosized morphology [60]. Two reduction peaks occur at about 2.58 and 1.37 V during the
first discharge, which suggest multiple inequivalent sites for lithium insertion into MnO₂ tunnels. The second cycle and subsequent ones differ notably from the first one with cathodic peaks shifted to higher voltage at 2.85 and 1.73 V. The voltage shift is very small for the anodic peak at the second cycle indicating a stabilization of the insertion/extraction mechanism in K₀.₀₃MnO₂ host lattice. Poyraz et al. [39] demonstrated that cathodic-anodic peak positions and the peak separations depend on the K⁺ content in the tunnels. Sample with high K⁺ content have smaller initial discharge capacities compared to low K⁺ containing sample. The initial electrochemical modification (1st cycle) is assigned to the “Li-cell formation” with the structural change that results from the so-called “loss of lithium inventory” [61]. A fraction of the Li⁺ ions inserted during the first discharge remains trapped in the tunnel structure. Both structural K⁺ and trapped Li⁺ ions stabilize the MnO₂ framework for the second and further discharge-charge cycles. The inserted Li⁺ ions occupying the 8h and 8h’ Wyckoff sites of the tetragonal lattice requires different energies of formation [62].

![Figure 5](image_url)

**Figure 5.** (a) Cyclic voltammograms of α-K₀.₀₃MnO₂ nanoneedles recorded at scan rate of 0.1 mV s⁻¹ in the voltage range from 1.0 to 4.0 V. (b) Voltage profiles of a K₀.₀₃MnO₂ NNS||Li cell over 50 cycles carried out at 30 mA g⁻¹. (c,d) Incremental discharge capacity at the first and second cycles showing the electrochemical transformation after the first lithiation process.

However, during the first cycle, the cathodic peak shift has been observed by several workers, but the reason for such trend is not exactly clear [20,63,64]. The shift of the initial cathodic peak in K₀.₂₅MnO₂ at about 2.22 V vs. Li⁺/Li toward higher potential in subsequent cycles was reported by Zhang et al. [20]. Some local restructuring or activation taking place during the initial Li insertion was conjectured. Two options can be considered. (i) As a part of Li is trapped in the KₓMnO₂ lattice, more Mn³⁺ ions remain at the end of the redox process. Mn³⁺ is a Jahn–Teller ion, which induce a lattice distortion and, consequently, a change in the Mn⁴⁺/³⁺ redox potential. (ii) The redox potential shift could be due to the reduction of Mn³⁺/Mn⁴⁺. Let us consider the standard potentials Mn⁴⁺/Mn³⁺ and Mn³⁺/Mn²⁺ redox reactions in solids. For aqueous systems, the MnIVO₂ → Mn³⁺ → Mn²⁺ redox reactions occur at the standard potential of 0.96 and 1.51 V vs. NHE, respectively. Mn³⁺/Mn⁴⁺ displays an oxidation potential at 0.8 V vs. RHE in perovskites. Spinel materials containing Mn³⁺ and Mn²⁺ also
exhibit high activities at 0.8 V vs. RHE. The reduction of β-MnO2 and the formation of Mn3O4 (with tetrahedral Mn2+ and octahedral Mn3+) occurs at 0.70 V vs. RHE. For aprotic systems, the lithium pyrophosphate Li2MnP2O7 and LiMnPO4 olivine display a Mn3+/Mn2+ redox potential centered at 1.17 and 0.82 V vs. SCE, respectively. Wang et al. [65] reported the redox reactions between Mn species in MnO2: the anode and cathodic peaks at 0.45 and 0.22 V vs. SCE are assigned to the Mn4+/Mn2+ reaction, while 0.0 and –0.25 V are the anodic and cathodic peaks of the Mn3+/Mn2+ reaction. Thus, the difference in the cathodic peak positions of 0.47 V is higher than the potential shift (0.27 V) observed in our voltammograms.

The oxidation process occurs with the appearance of corresponding anodic peaks at 2.90 and 2.38 V. The overlapping of the charge–discharge profile of the second cycle with subsequent ones implies a good reversibility. Similar electrochemical features have been observed previously for K0.25MnO2 [20]. In addition, the peak separation voltage (polarization) between Eox (2.85 V) and Ered (2.58 V) is ΔE = 0.27 V in the first cycle, but diminishes to as low as 0.05 V in forthcoming cycles, which is the other good evidence for high reversibility of as prepared α-Ky MnO2. Furthermore, the good reversibility is due to the presence of K+ ions within the 2 × 2 tunnels of the α-MnO2 structure maintained stable towards Li insertion and extraction during cycling. The excellent redox reversibility in the electrode is also demonstrated by the equal charge calculated by integration of the area under the reductive (discharge) and oxidative (charge) CV peaks. It is worthy to note that the polarization ΔE of 50 mV at a sweep rate of 0.1 mV s⁻¹ for K0.05MnO2 NNS is smaller than ΔE = 170 mV of α-MnO2 synthesized by acid digestion of Mn2O3 powders, due to the higher electronic conductivity of K-doped MnO2 [66] and the fast diffusion kinetics of Li⁺ ions [67]. It was also mentioned that ΔE is irrespective of the degree of structural order [27]. Moreover, the peak current Ip vs. scan rate ν⁻¹/² plot shows a linear behavior, which corresponds to a diffusion-controlled process.

Figure 5b shows the galvanostatic charge-discharge curves of the α-K0.03MnO2//Li cells cycled in the voltage range of 1.5–4.0 V at constant current density of 30 mA g⁻¹ at 25 °C. We can observe a slow decrease of the cell voltage with the presence of two pseudo-plateaus, which are evidenced as an S-shaped profile indicating a topotactic reaction for the Li insertion in the MnO2 framework, in which two inequivalent sites are available to coordinate Li⁺. Furthermore, the electrochemical behavior observed in CV measurement is confirmed by GCD experiment. There is a notable difference between the first discharge profile and forthcoming ones with a shift of plateaus to higher potential starting from the second cycle. The material also exhibits a capacity loss in initial four cycles from 211 to 198 mAh g⁻¹. The Faraday yield of 0.68 F mol⁻¹ for MnO2 is consistent with the mean oxidation state +3.885 for Mn ions determined by elemental analysis assuming an equal number of K⁺ and Mn³⁺ cations.

The pronounced changes in the electrochemical profile of the second cycle have been reported several times [20,27,56,68–70]. Different hypotheses have been conjectured: (i) A local activation can take place during the initial lithium insertion on the off-center 8h and 8h’ Wyckoff position (near the walls of the 2 × 2 tunnels), (ii) an ion-exchange reaction inducing a partial extraction of potassium from the centered 4e site, and (iii) a fraction of inserted lithium ions become trapped within the crystal structure of MnO2 during the first charge that enhances the lattice stabilization. Johnson [71] assigned the increase in voltage plateaus after the first cycle to a decrease in the cell impedance that occurs during cycling of α-MnO2 prepared by the acid digestion of Mn2O3 by H2SO4 but did not justify this claim by complementary experiments. Considering the small amount of K⁺ ions, the pronounced change in electrochemical behaviors in the second cycle (vs. the first cycle) could be signed to the difference in the site occupation by Li⁺ ions rather than the ion exchange in our sample. Recently, the CV peak shift during first scans has also been observed in the Li-Ky MnO2 system due to the irreversible local activation in the intercalated lattice and the formation of the solid interphase (SEI) layer [27,72].

Figure 5c,d show the incremental capacity curves (IC) (i.e., differential capacity vs. cell voltage (dQ/dV), of the first and second lithiation processes). This analysis can be considered as an efficient tool to determine the electrochemical spectroscopy of an electrode [73]. For instance, IC has been successfully applied to analyze the behavior of doped or blended cathodes [74,75]. The IC curves

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were extracted from the GCD profiles (lithiation process) to further characterize the electrochemical behavior at the first and second cycles showing the transformation after the first lithiation process. Each plot displays two broad peaks in the voltage range of 1.5–3.0 V corresponding to the plateaus in GCD curves. These results show clearly the upward potential shift after the first cycle, which indicate a change of the Li location in the host K₀.₀₃MnO₂ framework.

The rate capability and cycling stability of the α-K₀.₀₃MnO₂ electrode were tested in the voltage range 1.5–4.0 V at various current densities in the range 0.1–10 C. Results are presented in Figure 6a–c. Upon the increase of the current density, we observe a decay in the specific capacity without significant change of the charge and discharge profiles (Figure 6a). The S-shaped profile is maintained in the tested C-rate range. As shown in Figure 6b, the modified Peukert plot (i.e., discharge capacity vs. C-rate) exhibits an almost semi-logarithmic behavior, and the α-K₀.₀₃MnO₂ electrode delivers a specific capacity of ~32 mAh g⁻¹ at 10 C. Figure 6c presents the cycling performance of the α-K₀.₀₃MnO₂ electrode carried out at 30 mA g⁻¹ up to 100 cycles. Except for the first few cycles, the capacities decrease steadily. The fade rate of 0.3 mAh g⁻¹ per cycle for α-K₀.₀₃MnO₂ NNs electrode is much smaller than that for the unstabilized α-MnO₂ (2.3 mAh g⁻¹ per cycle) [68]. This behavior is similar to that observed for KMn₁₈O₆₄ nanofibers [20] and for KMn₁₆O₅₆ nanorods [26]. The good reversibility of the α-K₀.₀₃MnO₂ NNs is evidenced by the relevant coulombic efficiency that remains around 98.8% after several cycles. Considering the satisfying electrochemical stability, it seems that the cationic exchange (i.e., Li⁺ vs. K⁺) is negligible during the Li insertion in the α-K₀.₀₃MnO₂ framework.

**Figure 6.** (a) Voltage profiles (2nd cycle) of the K₀.₀₃MnO₂||Li cells at various C-rates. (b) Modified Peukert plot in the range 0.1 to 10 C. (c) Cycling stability of the K₀.₀₃MnO₂||Li cell obtained at 0.1 C.

4. Discussion

Although the application of cryptomelane KₓMnO₂ nanoparticles have been widely investigated in supercapacitor, to the best our knowledge, there is a limited number of studies devoted as cathode materials in LiBs [20,26,60,72–77]. In this work, the nanostructured cryptomelane-type KₓMnO₂ has been successfully prepared by the reduction of MnO₄⁻ ions in acidic medium at room temperature. Nanoneedles are well formed even within a short reaction duration of 1 h. A lot of literature has been reported on the synthesis of nanoparticle α-MnO₂ based materials, a brief summary is given here. Gao and Norby reported that the growth of α-MnO₂ nanofibers started after 30 min as a mixture of birnessite and cryptomelane phase via hydrothermal route at 140 °C. Relatively pure cryptomelane nanofibers would only be obtained after a reaction time of ~4 h [37]. Single-crystal α-MnO₂ nanowires (average diameter of 30 nm) were synthesized by only using potassium permanganate and sodium nitrite (molar KMNO₄:NaNO₂ ratio of 2:1) in acidic solution, while nanorods (50–100 nm diameter) were formed for decreasing molar ratio to 2:5 [78]. Similar MnO₂ nanoneedles with diameter of 10–50 nm and length of 200–500 nm were prepared by a two-step synthesis at temperature of 83 °C with a more complex procedure using MnCl₂·4H₂O, isopropanol and KMnO₄ raw materials [16].

Excellent properties of α-KₓMnO₂ have been obtained using a much simple synthesis process, in which the biologic reducing agent allows shorter reaction duration in ambient conditions. Let compare our material with others. Cryptomelane-type K₀.₁₀₆Mn₂O₄ nanoneedles were prepared
via a template-free, one-step hydrothermal method (HTM) using a complex chemistry composed of manganese(II) acetate tetrahydrate (MnAc$_2$·4H$_2$O) 99%, oxone monopersulfate compound (triple salt 2KH$_2$SO$_4$·KHSO$_4$·K$_2$SO$_4$), and potassium nitrate (KNO$_3$). Needle-like samples were obtained by HTM at 200 °C for 20 h [38]. Similar process was employed to prepare K$_{0.25}$Mn$_2$O$_4$ nanofibers with high potassium content with diameters in the range of 10–20 nm [20]. Liu et al. demonstrated that the size of nanoneedles can be controlled by cross-linking reagents (e.g., polyvinyl acetate (PVA), glycerol and glucose); the shorter K$_{0.3}$Mn$_2$O nanocrystals were obtained using PVA [42]. Cheng et al. controlled the synthesis of α-MnO$_2$ NWs using a hydrothermal method, in which potassium permanganate is reduced by acetic acid. The NWs with a length about 6–10 mm and an average diameter of 20 nm were obtained using 3 mmol KMnO$_4$ dissolved in 0.4 mol L$^{-1}$ CH$_3$COOH solution (30 mL) [79]. Li et al. succeeded to grow α-MnO$_2$ nanowires (width of ~30 nm and length of ~10 μm) with exposed (110) crystal plane using KMnO$_4$ and NH$_4$F in hydrothermal conditions but did not report the presence of tunneled K$^+$ ions [80].

The nanoneedles morphology of α-K$_x$MnO$_2$ appeared to be favorable of enhanced electrochemical performance partly due to the modified lattice parameters (i.e., the expansion in the a-direction and the slight contraction in the c-direction without obvious change in volume). Similar results have been reported by Feng et al. for the urchin-like MnO$_2$ formed by the assembly of nanoneedles prepared in acidic conditions [81]. A second key issue is the specific surface area. The BET value of 161 m$^2$ g$^{-1}$ is greater than values reported for MnO$_2$ prepared by different methods [48–53]. BET surface area of 132 m$^2$ g$^{-1}$ was reported for mesoporous α-MnO$_2$ hollow urchins prepared by mild reaction route [52]. Similar results were reported for mesoporous α-MnO$_2$ nanorods synthesized by reduction of KMnO$_4$ with a triblock polymer assisted by sonication (i.e., a pore volume of 1.0 cm$^3$ g$^{-1}$ but smaller pore diameter of 13.5 nm) [23]. Specific surface areas varying in the range of 35–110 m$^2$ g$^{-1}$ for α-MnO$_2$ NWs were shown to be dependent on the growth conditions [21]. α-MnO$_2$ nanotubes with large surface area (226 m$^2$ g$^{-1}$) fabricated by exfoliation of α-MnO$_2$ nanoflowers exhibited enhanced lithium storage properties [54]. The morphology of our sample is different from the heavy K-doped MnO$_2$ with fiber-like morphology growing along the c-axis [82]. Dai et al. pointed out that only nanoneedles as short fibers are obtained because the weak stabilization of tunnels by low K$^+$ ions concentration in the tetragonal crystal [69]. As the growth of α-MnO$_2$ nanoparticles is time- and temperature-dependent, it is noteworthy that the use of extract of broccoli favors the formation of nanoneedle-shape. During the synthesis, the purple color of KMnO$_4$ disappeared quickly after less than 1 h at room temperature and nanoneedles with diameter of about 5 nm and length of about 100 nm were formed. On the contrary, for the synthesis of K$_{0.08}$MnO$_2$ from the reduction of KMnO$_4$ in sulfuric acid without chelating agent, the final product was obtained after a reaction at high temperature of 60 °C for longer duration of 8 h [53].

Several studies have demonstrated that introduction of K$^+$ ions in the cryptomelane structure maintains the integrity of the lattice and is suitable for improving electrochemical properties of α-MnO$_2$ when applying as the cathode material for LIBs [37–39,72,83]. There is a kind of effective pillaring effect in presence of large cations with an ionic radius of 1.51 Å for eight-coordinated K$^+$ ions. Tomsett and Islam performed a comprehensive ab initio study of Li insertion in hollandite α-MnO$_2$ but did not consider a lattice with K$^+$ ions in the tunnels [61]. However, there is a compromise in the choice of potassium concentration in the 2 × 2 tunnels of MnO$_2$. Due to the lattice expansion and the electron donation, higher concentration of K$^+$ ions not only improves the Li$^+$ diffusion coefficient ($D_{\text{Li}^+}$) and enhances the electronic conductivity by boosting electrons hopping via Mn$^{3+}$/Mn$^{4+}$ couples, but also reduces the specific discharge capacity because the addition of inactive K$^+$ ions. An enhanced $D_{\text{Li}^+}$ has been estimated from 2.8 × 10$^{-15}$ to 1.9 × 10$^{-12}$ cm$^2$ s$^{-1}$ when pure α-MnO$_2$ was doped with 0.25 K$^+$ ion per formula [77]. Bach et al. [84] calculated a value of $D_{\text{Li}^+} \approx 10^{-10}$ cm$^2$ s$^{-1}$ for the hydrated α-phase K$_{0.062}$MnO$_2$ using cyclic voltammetry. Recently, using electrochemical impedance spectroscopy, Abuzeid et al. reported $D_{\text{Li}^+}$ values of 5.2 × 10$^{-11}$ and 2.1 × 10$^{-11}$ cm$^2$ s$^{-1}$ for K$_{0.11}$MnO$_2$ and K$_{0.08}$MnO$_2$, respectively, showing the diffusivity enhancement with the higher content of K$^+$.
ions [27]. Meanwhile, different synthetic approaches provide nanostructured cryptomelane-type MnO$_2$ with different particle shapes, particle sizes and particle size distributions [85,86]. Additionally, it has been achieved that nanoneedles or nanowires can accommodate large strain without pulverization and exhibit short lithium insertion pathways [87,88].

The $\alpha$-K$_y$MnO$_2$ nanoneedle-like material reported herein synthesized with the assistance of extract of broccoli plant as reducing agent with a small concentration of potassium has shown excellent electrochemical performances. However, the use of nanoneedles as electrode requested careful fabrication. It is worth noting that the composite hardly adheres to the Al foil during the electrode coating. This may attribute to the rather soft aluminum foil and the weak interaction between the very fine MnO$_2$ nanoneedle and aluminum (i.e., van der Waals forces). Thus, the preparation of $\alpha$-K$_y$MnO$_2$ electrode with ultra-high mass loading would be difficult and calls for the further study.

It is well known that the discharge capacity of $\alpha$-K$_y$MnO$_2$ comes from the insertion of lithium ions on available empty sites inside the (2 × 2) tunnels, i.e., off-center 8h Wyckoff positions [61] with the electrochemical reaction of K$_y$MnO$_2$ + xLi$^+$ + xe$^-$ $\rightarrow$ Li$_x$K$_y$MnO$_2$. However, the real situation seems to be more complex due to the presence of K$^+$ ions in the MnO$_2$ tunnels. We observed a drastic change of the discharge voltage profile after the first cycle. Such a behavior has been revealed by several reports on $\alpha$-MnO$_2$ materials with different tunneled cations [89,90]. After the formation, the voltage plateau remains stable at 2.88 V for our nanoneedle-like samples and is slightly higher than 2.80 V for K$_{0.00}$MnO$_2$ reported by Poyraz et al. [39], who showed that the discharge plateau voltage decreases systematically with increasing K$^+$ concentration (i.e., 2.62 V for K$_{0.04}$MnO$_2$). However, data of the literature are quite controversial showing the major influence of the central cation in the tunnel and the main role of the material morphology. In the early work, Rossouw et al. [91] observed CV curves with two well-resolved steps during cathodic and anodic scans, while Hill et al. [70] revealed a unique broad anodic peak during charge for nanofibers (~15–25 nm in diameter), for which the cathodic peak slightly shifted from 2.82 to 2.90 V. Dai et al. reported also changes in the CV curves in cryptomelane-type hydronium-doped MnO$_2$ (i.e., (H$_2$O)$_{0.10}$MnO$_2$·0.3H$_2$O) upon Li insertion that implies similar free energies for the different hosting Li sites after several cycles [68]. Johnson et al. [89] indicated the disappearance of the voltage plateau-type shape at about 2.5 V for lithia-stabilized $\alpha$-MnO$_2$ (i.e., $\alpha$-(Li$_2$O)$_{0.143}$MnO$_2$), while the discharge profile change is less pronounced for ammonia-stabilized sample (i.e., $\alpha$-(NH$_3$)$_3$MnO$_2$). Kijima et al. confirmed the loss of the plateau with cycling of $\alpha$-(Li$_2$O)$_{0.12}$MnO$_2$) [90]. This group demonstrated initial discharge capacity improvement by stabilizing the structure with chemical insertion of two Li-ions per unit cell. Zhang et al. reported the electrochemical performance of $\alpha$-K$_{1.0}$MnO$_{16}$ synthesized by hydrothermal route at 120 $^\circ$C that showed a voltage plateau at ca. 2.3 V and an initial discharge capacity of 360 mAh g$^{-1}$ at current density of 0.1 A g$^{-1}$. A non-negligible amount of K$^+$ ions were extracted from the K$_{1.0}$MnO$_{16}$ nanofibers cathode in the first charge reaction but showed a Coulombic efficiency of ~50% at C/3 rate [20]. Similar conclusion was claimed for the electrochemical reactions KMnO$_{16}$ nanorods [26]. In contrast, Ranjusha et al. [60] observed GCD single sloped curve without distinct voltage plateau for well-crystallized MnO$_2$ nanowires (30 nm in diameter) prepared by oxidation of Mn$^{2+}$ by MnO$_4$ and an initial capacity of 251 mAh g$^{-1}$ at C/2 rate but the K$^+$ content was not mentioned. Kumakai et al. demonstrated a two S-shaped discharge behavior with plateaus at 2.6 and 2.3 V for K$_{0.72}$Mn$_{8}$O$_{16}$ prepared by hydrothermal method at 80 $^\circ$C [76]. They stated that, in $\alpha$-K$_y$MnO$_2$ and its Co-doped specimen (K$_y$Mn$_{0.88}$Co$_{0.12}$O$_2$), the Li is inserted into two types of empty sites of the small (1 × 1) and large (2 × 2) tunnels with an initial discharge capacity of 250 mAh g$^{-1}$ at 10 mA g$^{-1}$.

Table 1 compares the electrochemical performance of the nanoneedle-like $\alpha$-K$_y$MnO$_2$ prepared in this work to previous reported cryptomelane-type $\alpha$-K$_y$MnO$_2$ cathode materials. In the early work by Ohzuku et al. [92], K$_y$Mn$_8$O$_{16}$ cathode materials prepared by two different methods showed S-shaped discharge curves with the relatively high voltage plateaus at 3.0 and 2.45 V. Sol–gel K$_{1.2}$Mn$_{8}$O$_{16}$ and acid digestion K$_{1.3}$Mn$_{8}$O$_{16}$ exhibit modest initial discharge capacities of 160 and 188 mAh g$^{-1}$, when cycled at 50 mA g$^{-1}$, respectively, due to the micrometer-sized particles [91]. Similar results were
obtained for heavy doped α-K$_y$Mn$_8$O$_{16}$ nanorods ($y \approx 1$, with a diameter of 5–15 nm and a length of 50–300 nm) synthesized using a reflux method with capacity of 159 mAh g$^{-1}$ at 50 mA g$^{-1}$ [26]. A comparison between K$_{0.25}$MnO$_2$ prepared by hydrothermal method at 160 °C and MnO$_2$ obtained by acid digestion (HNO$_3$ treatment) of the K-doped material shows specific discharge capacities of 143 and 170 mAh g$^{-1}$ at current density of 0.1 A g$^{-1}$, while in terms of cyclability, the capacity retention of 62% at 5 C rate is better for K$_{0.25}$MnO$_2$ than for the undoped cathode [74]. The Co-doped hydrothermal product K$_{0.14}$Mn$_{0.9}$Co$_{0.1}$O$_2$ from MnSO$_4$ and K$_2$S$_2$O$_8$ solution showed higher initial discharge capacity 180–200 mAh g$^{-1}$ at 50 mA g$^{-1}$ [93]. After 200 cycles the hydrated K$_{0.84}$Mn$_{0.16}$O$_{16}$·0.25H$_2$O nanowire-type electrode material fabricated by thermal regeneration process of MnO$_2$ waste delivered a specific capacity of 120 mAh g$^{-1}$ at 50 mA g$^{-1}$ [94]. K$_y$MnO$_2$ nanorods (100 nm in size) prepared by template-based sol-gel method delivered an initial discharge capacity of 183 mAh g$^{-1}$, which stabilized on subsequent cycles to 134 mAh g$^{-1}$ [95]. Urchin-like α-K$_{0.03}$MnO$_2$ formed by nanoneedles synthesized by sol-gel assisted by a redox reaction between ascorbic acid and KMnO$_4$ showed an outstanding initial specific capacity of 230 mAh g$^{-1}$ and 45% capacity retention at cycle one hundred [96]. Compared to the state-of-art of MDO materials, the cryptomelane-type α-K$_y$MnO$_2$ cathode prepared via biological reducing agent (broccoli extract) assisted synthesis shows good electrochemical performance.

| Composition | Morphology (Synthesis) | Specific Capacity (mAh g$^{-1}$) | Current Density (mA g$^{-1}$) | Ref. |
|-------------|------------------------|---------------------------------|-------------------------------|------|
| K$_y$MnO$_2$ | NRs (H)                | 189                             | 50                            | [68] |
| K$_{0.08}$MnO$_2$ | NNs (R)                | 236                             | 10                            | [27] |
| K$_{0.11}$MnO$_2$ | NNs (H)                | 198                             | 10                            | [27] |
| K$_{0.14}$MnO$_2$ | NNs (H)                | 160                             | 50                            | [93] |
| K$_{0.14}$Mn$_{0.9}$Co$_{0.1}$O$_2$ | NNs (H)              | 200                             | 50                            | [93] |
| K$_{0.25}$MnO$_2$ | NWs (H)                | 143                             | 100                           | [77] |
| K$_{0.125}$MnO$_2$ | NRs (Ox)              | 160                             | 50                            | [26] |
| K$_{0.84}$Mn$_{0.16}$O$_{16}$·0.25H$_2$O | NWs (Rc)          | 120                             | 50                            | [94] |
| K$_y$MnO$_2$ | NRs (R)                | 183                             | 10                            | [95] |
| K$_{0.04}$MnO$_2$ | NNs (R)                | 230                             | 30                            | [96] |
| K$_{0.32}$Mn$_{0.8}$O$_{16}$ | NFs (H)               | 200                             | 50                            | [39] |
| K$_{0.75}$Mn$_{0.25}$O$_{16}$ | NFs (H)              | 165                             | 50                            | [39] |
| K$_{0.25}$Mn$_{0.75}$O$_{16}$ | NKs (R)               | 260                             | 50                            | [67] |
| K$_{0.125}$MnO$_2$ | NFs (H)                | 190                             | 100                           | [20] |
| K$_{0.03}$MnO$_2$ | NNs (R)                | 210                             | 30                            | this work |

* a—hydrothermal; R—redox reaction; Ox—oxidation of Mn$^{2+}$; Rc—MnO$_2$ recycling.

5. Conclusions

In this work, one-dimensional α-K$_y$MnO$_2$ nanoneedles in pure cryptomelane phase were successfully prepared by a facile, one pot, scalable and environmentally-friendly method. An alternative biological reducing agent, i.e., extract of broccoli plant, was used instead of a traditional chemical chelate. This green-synthesis route is a straightforward and inexpensive facilitating mass production of nanostructured α-MnO$_2$ particles stabilized by potassium ions without templates. The nanostructure characterized by crystallite of 4.4 nm, large surface area 160.7 m$^2$ g$^{-1}$, high porosity and low potassium content of 0.03 per formula in the 2 × 2 tunnels favors good electrochemical performance. Electrochemical tests show an initial capacity ca. 211 mAh g$^{-1}$ with high Coulombic efficiency of 99% and good reversibility with a capacity retention 82% after 100 cycles. Thus, α-K$_{0.03}$MnO$_2$ nanoneedle-shaped material synthesized via the broccoli-extract-assisted green process could be considered as a promising cathode for LiBs.
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