



Manganese silicate hollow spheres enclosed in reduced graphene oxide as anode for lithium-ion batteries

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ABSTRACT

Herein is presented a new composite material consisting of nanostructured Mn silicate hollow spheres enclosed in a matrix of reduced graphene oxide (rGO), synthesized via a facile and low-cost hydrothermal method. The hollow structure provides free space to accommodate the volume expansion occurring upon lithiation, while the rGO facilitates the electron transport, thus enhancing the lithiation kinetics. Remarkably, the composite provides a continuously increasing reversible capacity up to ca. 1300 mAh g⁻¹ after 350 cycles. This increase in capacity is ascribed in part to the steadily rising fraction of Mn²⁺/Mn³⁺ being oxidized to Mn⁴⁺ as well as the reversible formation of the solid electrolyte interphase. The particle morphology, in fact, remains unaltered, as evidenced by *ex situ* scanning electron microscopy – even after 350 cycles. Additionally, the implementation of manganese as transition metal for the reversible conversion reaction appears advantageous with regard to the overall electrochemical performance and the relatively lower lithiation potential.

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1. Introduction

Lithium-ion batteries (LIBs) are the power source of choice for portable electronic devices and large-scale applications as, for instance, electric vehicles and stationary storage since they provide several favorable characteristics, such as high gravimetric and volumetric energy densities, high coulombic efficiency and long cycle-life [1,2]. However, the market demands batteries with better performance in order to realize the so-called electric-vehicle revolution [3] and eventually a green grid [4], targeting the reduction of fossil fuel consumption and CO₂ emission. Accordingly, today's LIBs require further improvement in terms of energy and power density. Commercial LIBs mostly employ natural and synthetic graphite anodes [5,6], which are characterized by a relatively high theoretical gravimetric capacities (372 mAh g⁻¹), but volumetric capacities of only about 750 mAh cm⁻³. As these values are practically achieved in commercial cells, advances in energy density can only be realized by developing new anode materials [6].

With respect to the lithium storage mechanism, there are mainly two alternative material classes [7]: alloying compounds, like silicon [8–10] or tin [11–15], and conversion materials, including transition metal oxides [16–20], nitrides [21–23], fluorides [24,25], and phosphides [26–28]. Recently, also transition metal silicates were proposed as alternative anode materials. Following the first study on cobalt silicate [29] synthesized by a conventional solid-state method and revealing specific capacities of more than 650 mAh g⁻¹ after 60 cycles, a plethora of silicates with varying (transition) metals has been reported [29–33]. For example, Yang et al. synthesized Ni₃Si₂O₅(OH)₄ nanotubes, showing a discharge capacity of 227 mAh g⁻¹ after 21 cycles [32]. Wei et al. reported Cu silicate hollow spheres, providing a capacity of 890 mAh g⁻¹ after 200 cycles [30]. Beside a generally low electronic conductivity, particularly, silicates including cobalt, nickel, or copper, however, reveal a rather high average delithiation potential, which intrinsically limits the achievable energy density when employed in lithium-ion full-cells [7]. Moreover, the conversion reaction is commonly characterized by pronounced volume variations upon dis-/charge, which detrimentally affects the long-term cycling stability.

To address the latter issue, one strategy involves the design of

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material composites in which the active material is encapsulated in a carbonaceous matrix effectively buffering the volume changes and, thus, reducing their detrimental effect on the long-term cycling stability, while simultaneously enhancing the electron transport [34–40]. Among the various carbon allotropes used for this purpose, especially graphene has attracted considerable interest due to its high electronic conductivity, mechanical strength, and large surface area [41–45]. A second strategy employs the synthesis of nanostructured hollow particles, providing free internal space to accommodate the occurring volume variation and, at the same time, short lithium transport pathways [46,46–48].

The de-/lithiation potential, however, is an intrinsic characteristic of the active material and cannot be addressed *via* the design of advanced composites (apart from eliminating kinetically induced overvoltages) [7]. In this regard, manganese provides an advantageously lower redox potential compared to the earlier mentioned cobalt, nickel, and copper – besides being non-toxic, abundant, and less expensive. In fact, manganese oxides, for instance, reveal average discharge and charge potentials of about 0.5 and 1.2 V vs. Li^+/Li , respectively, i.e., significantly lower potentials than, e.g., cobalt or nickel oxides [49–56].

With respect to silicates, nonetheless, there are only very few reports studying their application as lithium-ion anodes. Bai et al. synthesized a carbon-coated Mn silicate, characterized, indeed, by a low de-/lithiation potential and good cycling stability, but the reversible capacity remained rather low with only 345 mAh g^{-1} , i.e., a value slightly lower than those achieved for graphite [31].

Following these considerations, we synthesized nanostructured manganese silicate hollow spheres enclosed in reduced graphene oxide (MS-rGO) using a facile and economic hydrothermal method. Such composite exhibits a reversible capacity of about 1300 mAh g^{-1} after 350 cycles and an enhanced rate capability compared to neat manganese silicate hollow spheres (MS). Remarkably, the particle morphology appears unaltered even after 350 full discharge cycles, while the fraction of $\text{Mn}^{2+}/\text{Mn}^{3+}$ oxidized to Mn^{4+} upon charge is increasing during cycling.

2. Experimental

2.1. Synthesis of MS-rGO and MS

In a typical synthesis, SiO_2 beads were prepared by a modified Stöber method [57]. Graphene oxide (GO) was synthesized *via* a modified Hummer's method [58]. Subsequently, 1.60 mmol of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (ACROS, 99.999%) were dissolved in 17 mL of deionized water in a 40 mL Teflon liner. The earlier prepared SiO_2 beads (100 mg), dispersed in 10 mL of deionized water *via* sonication for 30 min , were added drop-wise into the Teflon liner and the resulting mixture was stirred for 15 min . Then, 5 mL of the aqueous GO suspension (ca. 2.0 g L^{-1}) were slowly added to this mixture and further stirred for 30 min . Finally, the suspension was transferred to a stainless steel autoclave (BERGHOF BR-40) and heated at $200 \text{ }^\circ\text{C}$ for 18 h under stirring (1000 rpm). After cooling to room temperature, the precipitate (MS-rGO) was washed several times with deionized water and ethanol and dried at $60 \text{ }^\circ\text{C}$ overnight. The neat MS were synthesized by the same method without adding rGO.

2.2. Structural and morphological characterization

The crystalline structure of the materials was investigated *via* powder X-ray diffraction (XRD) using a Bruker D8 Advance ($\text{Cu-K}\alpha_1$ radiation, $\lambda = 0.154 \text{ nm}$). The sample morphology was characterized by means of scanning electron microscopy (SEM, Zeiss LEO 1550VP) and transmission electron microscopy (TEM, JEOL JEM-

3000). For the *ex situ* SEM characterization, the cycled cells were disassembled in an argon-filled glove box (MBraun UNILab, H_2O and O_2 content $< 0.1 \text{ ppm}$). The electrodes were rinsed with dimethyl carbonate (DMC) to remove electrolyte residues. TGA (TA Instruments Q5000) was performed at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ under O_2 atmosphere. Raman spectra were collected with a He–Ne laser (633 nm) using Renishaw 2000, equipped with a He–Ne laser (633 nm). The specific surface area was determined by means of nitrogen gas adsorption based on the Brunauer-Emmett-Teller (BET) method, utilizing an Autosorb-iQ (Quantachrome).

2.3. Electrochemical characterization

The overall electrode composition was 70 wt\% active material, 20 wt\% conductive carbon (Super C65[®], TIMCAL), and 10 wt\% sodium carboxymethyl cellulose (CMC, Dow Wolff Cellulosics). For the slurry preparation, CMC was dissolved in ultrapure water (1.25 wt\% solution). Subsequently, Super C65 and the active material were added to the solution and ground in an agate mortar for 1 h . The obtained slurry was cast on dendritic copper foil (Schlenk, 99.9%) with a wet film thickness of $120 \text{ }\mu\text{m}$ using a laboratory doctor blade. The coated copper foil was dried overnight at room temperature. Disc-shaped electrodes ($\phi = 12 \text{ mm}$) were cut and dried under vacuum at $120 \text{ }^\circ\text{C}$ for 24 h . The electrode active material mass loading was around 1.5 mg cm^{-2} .

The electrochemical performance was evaluated either in stainless steel 2032 coin cells or Swagelok-type T-cells using lithium foil (Rockwood Lithium, battery grade) as counter and reference electrodes. The electrolyte consisted of a 1 M solution of LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 by volume, UBE; 1 wt\% of vinylene carbonate (VC) added). Cells were assembled in an argon-filled glove box (MBraun UNILab, H_2O and O_2 content $< 0.1 \text{ ppm}$). Prior to the electrochemical characterization, the cells were allowed to rest for 6 h . Cyclic voltammetry (CV) was performed utilizing a potentiostat (VMP3, BioLogic), setting the reversing voltages to 0.01 and 3.0 V vs. Li^+/Li . Galvanostatic cycling (GC) tests were carried out by means of a battery tester (Maccor 4300), setting the cut-off voltages to 0.01 and 3.0 V vs. Li^+/Li . All electrochemical measurements were performed in hermetic climatic chambers at a temperature of $20 \pm 1 \text{ }^\circ\text{C}$. It is important to note that the mass of reduced graphene oxide in MS-rGO was included for the calculation of the specific capacity.

3. Results and discussion

3.1. Morphological and structural characterization

In Fig. 1, the SEM micrographs of the as-synthesized MS and MS-rGO samples are presented, including the EDX elemental mapping for manganese, silicon, oxygen, and carbon. The MS particles (Fig. 1a) nicely resemble the morphology of the SiO_2 precursor (Fig. S1), revealing a uniform spherical morphology with a mean particle diameter of about 400 nm . No indication of different particles morphologies could be detected, while the MS particles, as expected, show a rougher surface compared to the SiO_2 precursor. The EDX analysis confirms the presence and homogeneous distribution of Mn, Si, and O, as shown in Fig. 1b–e, while the carbon mapping (Fig. 1f) nicely illustrates the absence of carbon in or on the MS particles. In contrast, the SEM-EDX analysis of the MS-rGO sample (Fig. 1g to l) clearly reveals that rGO is covering the MS particles (see especially Fig. 1i), while the overall MS particle shape and composition is not altered by the presence of rGO in the hydrothermal synthesis using an autoclave. The preferred presence of rGO on the MS particle surface and their hollow nature are more-over confirmed by means of TEM (Fig. 2), exhibiting a thickness of

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