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Published in:
Energy Technology

DOI:
[10.1002/ente.201600459](https://doi.org/10.1002/ente.201600459)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Tillmann, S. D., Cekic-Laskovic, I., Winter, M., & Loos, K. (2017). Nickel Network Derived from a Block Copolymer Template for MnO₂ Electrodes as Dimensionally Stabilized Lithium-Ion Battery Anodes. *Energy Technology*, 5(5), 715-724. <https://doi.org/10.1002/ente.201600459>

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Nickel Network Derived from a Block Copolymer Template for MnO₂ Electrodes as Dimensionally Stabilized Lithium-Ion Battery Anodes

Selina D. Tillmann,^{*,[a]} Isidora Cekic-Laskovic,^[a] Martin Winter,^[a, b] and Katja Loos^[c]

To improve lithium-ion batteries further, novel concepts for the reproducible preparation of highly structured bicontinuous battery electrodes are required. With this in mind, the main focus of this work is based on the block copolymer template-directed synthesis of metal nanofoams suitable for the rational study and design of the final conductive matrix through molecular engineering of the starting polymer. As a proof of concept, diverse MnO₂ electrodes with nickel foam as substrates are prepared and morphologically and structurally characterized by means of SEM, Raman spec-

troscopy, and XRD. To investigate the electrochemical properties of the prepared MnO₂-nickel foam electrodes, cyclic voltammetry and galvanostatic cycling experiments, including C-rate tests, are performed and the obtained results are discussed with respect to the deposition time. Compared with the reference, namely, bulk MnO₂-nickel foil electrodes, superior electrochemical characteristics, particularly regarding C-rate capability and long-term cycling stability, are achieved, which is attributed to better dimensional stability of the composite electrode.

Introduction

Despite the fact that lithium-ion batteries (LIBs) have already entered the sustainable electric vehicle market, it is well known that improved state-of-the-art systems are still in demand.^[1,2] To improve the performance of these systems, nanostructured electrodes have been widely studied, as summarized in a review by Song and co-workers.^[3,4] Thus, a 3D approach to the overall design of electrodes involving an interpenetrating conductive pathway has been proposed as an optimal solution.^[5,6] Various attempts to realize 3D-structured electrodes have been made, including the construction of a polymer scaffold,^[7] nanostructured carbonaceous tubes and foams,^[8–11] and nickel networks/foams^[12–16] as a conductive matrix. A significant advantage of 3D metal structures over bulk electrodes lies in fixed electronic contact points with the active material. In addition, the rigid metal structure leads to reinforcement of the overall dimensional stability of the electrode, in particular, when the active electrode material shows pronounced shrinking and expansion with the state of charge (SOC). Accordingly, structural deterioration of the active material, leading to poor long-term cycling performance and rate capability, may be reduced by the incorporation of a conductive metal framework. However, a reproducible and tailor-made design of nanostructured metallic foams with specific dimensional properties is difficult to achieve with current techniques. Moreover, the prepared metal foams are typically highly disordered. Thus, effective stress cannot be redistributed from the ligament nanoscale to the overall macroscale, resulting in poor mechanical properties. Destruction of the active material can be reduced by employing the block copolymer template-directed synthesis of the metal nanofoams.^[17]

Block copolymers generally separate into microphases on a nanoscale level owing to the chemical incompatibility of different blocks. Hence, a variety of well-ordered 1D, 2D, or 3D periodic nanostructures, such as spheres, cylinders, gyroids, and lamellae, or even more complex structures, such as hexagonally perforated layers, can be obtained. Depending on the molecular weight of the constituent blocks, the self-assembled structures can be defined and tailored with nanometer accuracy to address the specific purposes of functional materials. In this manner, 3D electrodes interpenetrated by a conductive metal framework can be prepared with defined pore sizes and material loading and, subsequently, the morphology of the final battery electrode can be rationally designed and modified through molecular engineering of the block copolymer template.

Manganese oxide and its derivatives, which have mainly been used in primary lithium batteries^[18] and alkaline batteries,^[19,20] have attracted some attention as anode materials for

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LIBs in recent years, thanks to their high theoretical capacity (700–1000 mAh g⁻¹), low cost, environmental friendliness, and natural abundance.^[21–25] However, MnO₂ electrodes suffer from reduced cycle life due to large volume expansions/shrinkages during cycling, originating from poor electric conductivity through the bulk.^[26] In recent years, some attempts have been made to overcome structural deterioration of the active material. Nanostructured MnO₂ electrodes with architectures such as nanowires,^[23] -tubes,^[27] and -crystals^[28] have been reported. Furthermore, by “going nano” and simultaneously incorporating a long-range-ordered conductive metal framework, the overall electrode dimensional stability could be reinforced. Thus, prolonged cycle life and high-capacity LIB anodes can be achieved.^[29]

Herein, a concept of employing the manifold self-assembled morphologies of block copolymers for the preparation of 3D nanostructured battery electrodes is introduced. Bicontinuous gyroid nickel networks, derived from a high-molecular-weight block copolymer, are utilized as interpenetrating current collectors. As a proof of concept, 3D MnO₂ electrodes are prepared by an electrodeposition process and morphologically and structurally studied by SEM, Raman spectroscopy, and XRD. In addition, their electrochemical properties are validated by cyclic voltammetry and galvanostatic cycling experiments. First, the influence of the interpenetrating metal matrix on the rate capability and longevity is investigated. For these experiments, MnO₂ is plated on nickel foil to obtain a bulk electrode and on nickel foam to obtain an electrode with a 3D structure. In a second set of experiments, the influence of the plating time on the electrochemical properties of nickel-foam-based electrodes is evaluated.

Results and Discussion

Route to 3D bicontinuous electrodes from block copolymer templates

The synthetic route to tailor-made bicontinuous electrodes for applications in LIBs is outlined in Figure 1. Supramolecular complexes of polystyrene-*block*-poly(4-vinylpyridine)(3-pentadecylphenol) (PS-*b*-P4VP(PDP)) are taken as precursors for the formation of nanoporous nickel foams.

First introduced by Vukovic et al., this approach offers considerable advantages over previously described polymer template-directed synthesis of metal foams.^[30] The most striking advantage is the refined way of simply tuning the morphology of the overall template, PS-*b*-P4VP, by varying the addition of *x* (ratio between PDP molecules and P4VP monomer units) of a low-weight amphiphilic compound.^[31–33] After annealing of the polymer films (Figure 1a), the formation of an open network structure facilitates removal of the amphiphile. By immersing the complex in ethanol, a selective solvent for PDP, a hydrophilic surface suitable for direct processing of the polymer template is generated (Figure 1b). Thus, electroless plating can be employed to backfill the porous polymer template with the desired metal (Figure 1c), and subsequently, the remaining polymer is removed by pyrolysis. Well-ordered metal frameworks are exposed (Figure 1d) that act as scaffolds for the incorporation of suitable active materials through electrodeposition to finally obtain the desired 3D nanostructured electrodes (Figure 1e). Herein, the gyroid polymer template (Figure 2a) is derived from the supramolecular complex PP-190-64 ($M_n(\text{PS}) = 190 \text{ kg mol}^{-1}$, $M_n(\text{P4VP}) = 64 \text{ kg mol}^{-1}$) with $x(\text{PDP}) = 0.5$.

By utilizing the introduced preparation procedure, an inverse nickel replica is obtained upon removal of the additive, insertion of metal, and thermal degradation of the polymer matrix (Figure 2b). MnO₂ is chosen for backfilling of the porous nickel matrix through an electrodeposition process. To ensure uniform electrodeposition through the 3D porous metal, a pulse current program is applied. The 3D MnO₂ electrodes with varying plating times from 3 to 7 h are prepared. Electrodes with plating times of 3 and 6 h, respectively, are depicted in Figure 2c and d. In contrast to the first sample with a plating time of 3 h (Figure 2c), the deposit on the nickel foam is clearly visible after 6 h of deposition (Figure 2d). Pores are still present after a deposition time of 6 h. However, it appears that the pores of the nickel foam are completely filled with MnO₂ after a plating time of 7 h.

Structural and morphological characterization of the MnO₂ electrodes

Structural and morphological characterization of the MnO₂ electrodes is exemplarily performed for the MnO₂-nickel foil bulk sample by means of Raman scattering and XRD experi-

Figure 1. Route for the preparation of bicontinuous nanostructured electrodes. Starting with a) the supramolecular complex PS-*b*-P4VP(PDP) (PS in green, P4VP(PDP), in blue), b) the block copolymer template is generated upon removal of the amphiphile, which is followed by c) electroless plating of the polymer template with a suitable metal. Upon thermal degradation of the organic template, d) the metal foam is exposed, serving as a conductive framework for the incorporation of the active material to realize e) the final nanostructured electrode. Adopted from Ref. [17].

Figure 2. SEM micrographs of a) gyroid block copolymer template ($\times 25k$ magnification and inset $\times 50k$ magnification), b) gyroid nickel foam, c) MnO_2 -nickel foam electrode after 3 h of plating time, and d) MnO_2 -nickel foam electrode after 6 h of plating time (all $\times 25k$ magnification).

ments. In the Raman spectrum (Figure 3a), the strong band at 630 cm^{-1} can be assigned to the symmetric vibration of the Mn–O bond in the MnO_6 octahedra.^[34]

For further characterization, the corresponding XRD pattern of an electrode consisting of nickel foil and deposited MnO_2 is depicted in Figure 3b. Apart from the diffraction peaks corresponding to the nickel foil substrate, no additional peaks are observed. The absence of diffraction peaks indicates that the deposit is not crystalline. Thus, a predominately amorphous structure of the MnO_2 deposit can be concluded.

Electrochemical characterization of the MnO_2 electrodes

Cyclic voltammetry of MnO_2 foam and bulk electrodes

In the context of designing electrodes for applications in LIBs, the surface has a huge impact on the electrochemical performance of the overall electrode. In particular, nano-structured electrodes offer an increased contact area between electrode and electrolyte, which can reduce electrode polarization losses and offer improved power and energy density. However, the occurrence of unwanted side reactions between electrode and electrolyte, leading to irreversible capacity losses, due to electrolyte losses and solid–electrolyte interphase (SEI) formation, has to be taken into account as well.^[3,35] To validate the application of the prepared 3D MnO_2 -foam electrodes in LIBs, they were studied with respect to their electrochemical properties depending on the

Figure 3. Structural and morphological characterization of the prepared MnO_2 -nickel foil electrode: a) Raman spectrum and b) XRD pattern.

Figure 4. Cyclic voltammograms of a) bulk MnO_2 -nickel foil (after 96 h plating time) and b) MnO_2 -nickel foam electrode (after 7 h plating time). (Working electrode (WE): MnO_2 , counter electrode (CE) and reference electrode (RE): metallic lithium, electrolyte: 1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) 1:1 (w/w), potential range: 0.01–2 V versus Li/Li^+ , scan rate: 1 mVs^{-1}).

plating time and compared with reference bulk MnO_2 -nickel foil electrodes. Cyclic voltammograms of the reference bulk MnO_2 -nickel foil (after 96 h deposition) and MnO_2 -nickel foam electrode after 7 h of deposition are shown in Figure 4.

For both electrodes, the potential range from 0.5 to 1.5 V versus Li/Li^+ of the first reductive scan is strongly determined by the formation of the SEI. However, in the case of the MnO_2 -foam electrode (Figure 4b), the SEI formation process is more pronounced; this is caused by the immensely greater surface area of the nickel foam substrate (Figure 2b). Once the SEI layer is formed, further electrolyte decomposition is mostly inhibited (both cyclic voltammograms), as evidenced by the absence of the corresponding current responses in subsequent cycles. The initial cycle of the bulk MnO_2 -nickel foil electrode differs from those of subsequent ones (Figure 4a). The broad peak (1st cycle) located at 0.22 V versus Li/Li^+ shifts to more positive potential values of 0.37 V versus Li/Li^+ . Thus, the reduction of MnO_2 to metallic manganese is concluded.^[23,36] In the reverse scan, one main peak appearing at 1.15 V versus Li/Li^+ is attributed to the reversible oxidation of Mn^0 to Mn^{2+} . In the cyclic voltammogram of the MnO_2 -nickel foam electrode (Figure 4b), similar behavior can be identified. Although the SEI formation process overlaps with the initial reductive peak, peaks at 0.54 (oxidation) and 1.20 V versus Li/Li^+ (reduction) are present in subsequent cycles. Thus, reversible lithiation and delithiation of the as-prepared MnO_2 electrodes both on nickel foam and nickel foil substrates can be confirmed with regard to the distinct reductive and oxidative peaks.

Galvanostatic cycling experiments

To further investigate the electrochemical properties of the prepared MnO_2 electrodes, galvanostatic cycling is performed. However, to ensure comparable cycling results, the maximum capacity of each electrode is determined by a slow prelithiation/delithiation step. Based on the determined capacity, C , a current, I , is calculated, whereby I represents the

current that would theoretically correspond to 1C. Galvanostatic cycling is performed at 1I and a C-rate test is performed (3 cycles of each 2 and 5I and 5 cycles at 10I) to validate the C-rate capability of the prepared MnO_2 electrodes. Hereafter, the term 1st cycle refers to the first cycle after the cyclic voltammetry experiment and the prelithiation/delithiation cycle. The galvanostatic cycling results of the bulk MnO_2 and foam MnO_2 electrodes are depicted in Figure 5.

Thus, MnO_2 electrodes with nickel foil and nickel foam, both used as current collectors, are prepared with the intention of creating electrodes of comparable capacity. This is achieved when depositing MnO_2 for 7 (nickel foam) and 96 h (nickel foil). The porosity of the electrodes is determined to be 1.2% for the nickel-foil-based electrode and 3.2% for the nickel-foam-based electrode. Although the deposition time is five times longer in the case of the bulk electrode, the average delithiation capacity is only two times higher than that of the nickel foam electrode (Figure 5a). Table 1 illustrates the key electrochemical parameters of the galvanostatic cycling results at 1I. The 1st cycle Coulombic efficiencies of (64.5 ± 2.1) (MnO_2 -nickel foil electrode, 96 h deposition) and $(72.7 \pm 2.6)\%$ (MnO_2 -nickel foam electrode, 7 h deposition) with corresponding delithiation capacities of (0.0250 ± 0.0008) and $(0.0083 \pm 0.0003) \text{ mAh}$, respectively, are obtained.

As depicted in Figure 5b, both electrodes initially show similar delithiation capacity retention values. However, directly after the C-rate test, it appears that the capacity loss of the MnO_2 nickel foam electrode becomes smaller than the capacity loss of the bulk electrode. The MnO_2 nickel foam electrode seems to cope better with the C-rate test, and thus, the capacity can be better retained compared with that of the bulk material. In particular, from about the 80th cycle onwards, the difference between the two investigated electrodes becomes greater, leading to the 195th cycle capacity retention of $(50.6 \pm 1.8)\%$ compared with $(43.4 \pm 1.4)\%$ for the bulk material (compared with the 1st cycle). This effect might be attributed to the conductive metal framework,

Figure 5. Galvanostatic cycling of MnO₂-nickel foil bulk (96 h deposition) and MnO₂-nickel foam (7 h deposition) electrodes with plots of a) delithiation capacity and Coulombic efficiency versus cycle number and b) delithiation capacity retention versus cycle number. Inset in b) shows the delithiation capacity retention versus cycle number for the C-rate test. Values for capacity retention are calculated based on the distinct first cycle. After the cell capacity determination step, each electrode was cycled with a current rate of 1 I, followed by a C-rate test (3 cycles at 2 and 5 I, respectively, and 5 cycles at 10 I, inset) and constant current cycling at 1 I for an additional 155 cycles. (WE: MnO₂, CE and RE: metallic lithium; electrolyte: 1 M LiPF₆ in EC/DMC 1:1 (w/w), potential range: 0.01–2 V versus Li/Li⁺).

Table 1. Key parameters of electrochemically investigated MnO₂-nickel foil bulk (96 h deposition) and MnO₂-nickel foam (7 h deposition) electrodes during constant current charge/discharge cycling at 1 I after formation and capacity determination with cyclic voltammetry and prelithiation/delithiation, respectively. Given errors are based on the investigation of three MnO₂ electrodes.

Electrode	First cycle delithiation capacity [mAh]	Coulombic efficiency [%]	calculated delithiation rate	195th cycle Coulombic efficiency [%]	capacity retention based on 1st cycle [%]
MnO ₂ bulk (96 h)	0.0250 ± 0.0008	64.5 ± 2.1	0.5C	98.8 ± 3.2	43.4 ± 1.4
MnO ₂ foam (7 h)	0.0083 ± 0.0003	72.7 ± 2.6	1.2C	99.0 ± 3.6	50.6 ± 1.8

which apparently enables a reinforcement of the overall dimensional stability of the electrode. Hence, shrinkage and expansion of the active material with the SOC can be compensated for, leading to improved long-term cycling performance of the MnO₂-nickel foam electrode.

For detailed analysis of the C-rate capability, the respective region is enlarged in the capacity retention versus cycle

number plot (Figure 5b, inset) and the corresponding key electrochemical parameters are summarized in Table 2.

The given values correspond to the last cycle of the respective rate test. In addition to the shown capacity retentions, the corresponding applied delithiation current rates are given. Generally, considerably improved capacity retentions are observed for the nickel-foam-based electrode. For

Table 2. Key parameters of the C-rate test of MnO₂-nickel foil bulk (96 h deposition) and MnO₂-nickel foam (7 h deposition) electrodes. Given errors are based on the investigation of three MnO₂ electrodes.

Electrode	Calculated delithiation rate of the			Capacity retention [%]		
	33rd cycle (2 I)	36th cycle (5 I)	41st cycle (10 I)	33rd cycle (2 I)	36th cycle (5 I)	41st cycle (10 I)
MnO ₂ bulk (96 h)	3.6C	15.8C	20.9C	51.1 ± 1.6	29.4 ± 0.9	25.4 ± 0.8
MnO ₂ foam (7 h)	3.4C	12.3C	35.2C	62.0 ± 2.2	43.1 ± 1.6	30.1 ± 1.1

instance, by applying a current of 2 I (33rd cycle), capacity retentions of (62.0 ± 2.2)% at 3.4 C for the nickel foam and only (51.1 ± 1.6)% at 3.6 C for the bulk are obtained. In case of higher applied currents, namely, 10 I (41st cycle), the capacity retention of the foam-based electrode is superior to the foil-based one, although the C-rate was 1.75 times higher. Consequently, the conductive metal framework results, on one hand, in a dimensional stabilization of the overall MnO₂ electrode, leading to improved long-term cycling stability and, on the other hand, to enhanced rate capabilities.

After the interpenetrated MnO₂ electrode already showed improved galvanostatic cycling relative to the reference bulk MnO₂ electrode, nickel-foam-based electrodes are further evaluated as a function of the deposition time. Based on SEM investigations (Figure 2), electrodes with deposition times of 3 and 6 h and porosity values of 23.5 and 8.5%, respectively,^[37] are prepared and investigated with regard to their galvanostatic cycling performance. In Figure 6, the galvanostatic cycling results of the MnO₂-nickel foam electrodes with deposition times of 3 and 6 h are shown. For comparison, the results of the previously investigated MnO₂-nickel foam electrode after 7 h of deposition time with a porosity of 3.2% are included.

Figure 6a depicts the delithiation capacity and Coulombic efficiency versus cycle number plot, whereas the corresponding key parameters are summarized in Table 3.

Clearly, the overall cycling behavior of the investigated MnO₂-nickel foam electrodes depends on the deposition time. The 1st cycle efficiencies for the MnO₂-foam electrodes of (62.5 ± 2.4) (3 h deposition), (59.3 ± 2.3) (6 h deposition), and (72.7 ± 2.6)% (7 h deposition) with corresponding delithiation capacities of (0.1740 ± 0.0068), (0.0252 ± 0.0099), and (0.0083 ± 0.003) mAh, respectively, are achieved. As discussed above, longer deposition times do not necessarily correlate with capacity increase. Because the SEM investigations (Figure 2) revealed almost filled nickel foam pores

after a deposition time of approximately 6 h, electrolyte access of the 3D electrodes is therefore blocked. Lithium-ion diffusion might be a problem for thicker MnO₂ layers. Although more active material is present in the case of the MnO₂-nickel foam electrode with a deposition time of 7 h, less active material is accessible, resulting in lower absolute capacities than those of the foam electrodes after 3 and 6 h of deposition time.

Long-term cycling reveals a strong influence of the surface area on the electrochemical properties. In Figure 6b, the corresponding capacity retention versus cycle number plot of the nickel foam-MnO₂ electrodes is given. The 75th cycle capacity retentions (based on the 1st cycles) of (38.8 ± 1.5), (61.4 ± 2.4), and (61.7 ± 2.2)% are obtained for MnO₂ electrodes with 3, 6, and 7 h of deposition, respectively. Indeed, the MnO₂-foam electrode with 3 h of deposition time delivers the highest delithiation capacity values and constant electrolyte decompositions, and thus, continuous lithium loss seems to occur due to the high porosity of the electrode. This effect is reduced with increasing deposition time as MnO₂ fills the pores to a greater extent.

To evaluate the C-rate capability of the investigated MnO₂-foam electrodes, the corresponding region in the capacity retention versus cycle number plot (Figure 6b) is enlarged (inset) and the key parameters of the C-rate test are summarized in Table 4.

For thin-film electrodes, the influence of different C rates on the electrochemical performance is known to be rather small.^[38] However, the difference in thickness between the MnO₂ electrodes, although it is in the small nanometer range, seems to strongly influence the C-rate response. Among the nickel foam-MnO₂ electrodes, it appears that the electrode with the longest deposition time (7 h) shows the best capacity retention for the applied currents of 2, 5, and 10 I. Consequently, the electrochemical properties of the investigated nanostructured 3D electrodes appear as a trade-off between lithium-ion diffusion within the bulk active ma-

Table 3. Key parameters of electrochemically investigated MnO₂-nickel foam electrodes (3, 6, and 7 h deposition) during the constant current charge/discharge cycling at 1 I after formation and capacity determination by cyclic voltammetry and prelithiation/delithiation, respectively. Given errors are based on the investigation of three MnO₂ electrodes.

Electrode	1st cycle delithiation capacity [mAh]	Coulombic efficiency [%]	calculated delithiation rate	75th cycle	
				Coulombic efficiency [%]	capacity retention based on 1st cycle [%]
MnO ₂ foam (3 h)	0.1740 ± 0.0068	62.5 ± 2.4	0.1C	92.4 ± 3.6	38.8 ± 1.5
MnO ₂ foam (6 h)	0.0252 ± 0.0099	59.3 ± 2.3	0.4C	97.0 ± 3.8	61.4 ± 2.4
MnO ₂ foam (7 h)	0.0083 ± 0.0003	72.7 ± 2.6	1.2C	98.6 ± 3.5	61.7 ± 2.2

Figure 6. Galvanostatic cycling results of nickel foam-MnO₂ electrodes with deposition times of 3, 6, and 7 h: a) delithiation capacity and Coulombic efficiency versus cycle number plot and b) delithiation capacity retention versus cycle number plot for the C-rate test. Values for capacity retention are calculated based on the distinct first cycle. After the cell capacity determination step, each electrode was cycled with a current rate of 1 I, followed by a C-rate test (3 cycles at 2 and 5 I, respectively, and 5 cycles at 10 I, inset), and constant current cycling at 1 I for an additional 35 cycles. (WE: MnO₂, CE and RE: metallic lithium; electrolyte: 1 M LiPF₆ in EC/DMC 1:1 (w/w), potential range: 0.01–2 V versus Li/Li⁺).

Table 4. Key parameters of the C-rate test of electrochemically investigated nickel foam-MnO₂ electrodes (3, 6, and 7 h deposition). Given errors are based on the investigation of three MnO₂ electrodes.

Electrode	Calculated delithiation rate			Capacity retention [%]		
	33rd cycle (2 I)	36th cycle (5 I)	41st cycle (10 I)	33rd cycle (2 I)	36th cycle (5 I)	41st cycle (10 I)
MnO ₂ foam (3 h)	1786C	3571C	7692C	4.2 ± 0.2	4.1 ± 0.2	0.1 ± 0.0039
MnO ₂ foam (6 h)	52C	333C	909C	11.3 ± 0.4	4.1 ± 0.2	1.8 ± 0.07
MnO ₂ foam (7 h)	3.4C	12.3C	35.2C	62.0 ± 2.2	43.1 ± 1.7	30.1 ± 1.2

terial and the surface area of the electrodes. An increase in the porosity with prolonged MnO₂ deposition time from 3.2% (7 h) to 8.5 (6 h) and 23.5% (3 h) results in an extended passivation process of the electrode surface. The pronounced occurrence of side reactions leads to reduced Coulombic efficiencies. Simultaneously, the increased SEI layer thickness leads to reduced lithium-ion diffusion properties in the bulk, resulting in slower lithiation and delithiation of the

active material, and thus, a strongly reduced rate performance with increased electrode porosity.

In addition, potential versus capacity plots for lithiation and delithiation of the 1st and 30th cycles of the MnO₂ bulk (96 h deposition) and MnO₂ foam electrodes with 3, 6, and 7 h of deposition time are depicted in Figure 7.

For all electrodes a lithiation plateau at approximately 0.5 V versus Li/Li⁺ is present, which is in good agreement

Figure 7. Potential versus capacity plots of investigated MnO_2 electrodes (a) MnO_2 bulk electrode (96 h deposition) and MnO_2 nickel foam electrodes after 3 (b), 6 (c), and 7 h (d) deposition time, respectively. Constant current charge/discharge cycling is performed at 1-I after formation and capacity determination with CV and prelithiation/delithiation. (WE: MnO_2 , CE and RE: metallic lithium; electrolyte: 1 M LiPF_6 in EC/DMC 1:1 (w/w), potential range: 0.01–2 V versus Li/Li^+).

with the previously discussed cyclic voltammetry results.^[23] It appears that the plateau is more pronounced when higher amounts of active material are present. Furthermore, well-defined delithiation plateaus can be observed at about 1.1 V versus Li/Li^+ . Hence, it can be concluded that MnO_2 in the investigated electrodes is indeed electrochemically active for both lithiation and delithiation.

Bearing in mind that increasing the surface area of the electrodes leads to strongly increased irreversible capacities, the nickel foam- MnO_2 electrode with a deposition time of 7 h offered the best overall electrochemical performance, in particular, regarding C-rate capability. In addition, the nickel-foam-based MnO_2 electrode shows superior electrochemical performance compared with that of the reference bulk electrode. Nickel-foam-based electrodes present themselves as a promising candidate capable of satisfying the increasing demand for high energy and power density LIB electrodes.

Conclusions

A new concept of using block copolymer templates for the design of 3D bicontinuous electrodes was introduced and an electrochemical comparison between the as-prepared 3D MnO_2 and reference bulk electrodes was performed.

Various nickel foam- MnO_2 electrodes obtained after plating times ranging from 1 to 7 h were prepared through an electrodeposition process and the as-prepared electrodes were morphologically and structurally characterized by means of SEM, Raman spectroscopy, and XRD. Furthermore, the nanostructured electrodes were studied with respect to their electrochemical properties as a function of deposition time. Galvanostatic cycling experiments revealed a strong dependency of the electrochemical properties on the degree of deposition inside the foam structure. Finally, the nickel foam- MnO_2 electrode with a deposition time of 7 h showed clearly improved electrochemical characteristics relative to those of the reference bulk nickel foil- MnO_2 electrode, particularly regarding long-term cycling stability and rate capability.

Because this study serves as a proof of concept, further investigations, in particular, regarding the optimization of the polymer template by molecular engineering of the parent block copolymer are required. In this regard, the electrode's surface area may be reduced to compensate for surface-related electrolyte decomposition by using higher molecular weight diblock copolymers. In addition, changing the amount of amphiphile could yield many different polymer morphologies, such as lamellar or cylindrical. Thus, the influence of the 3D structure of the current collector on the electrochemical properties of an electrode could be investigated. In addition, this approach may be extended to further active materials, such as silicon or tin, for which electrodeposition is well studied.^[39–41]

Experimental Section

General

Supramolecular complexes of PS-*b*-P4VP(PDP)_x ($x=0.5$) with $M_n(\text{PS})=190 \text{ kg mol}^{-1}$ and $M_n(\text{P4VP})=64 \text{ kg mol}^{-1}$ (Polymer Source, Inc.) served as starting materials for the preparation of polymer templates, and subsequently, for the formation of nickel foams through electroless plating. The detailed synthetic procedures were described elsewhere.^[42] Unless otherwise noted, all further chemicals, received from Sigma–Aldrich, were used as received.

Preparation of MnO₂ electrodes by electrodeposition

MnO₂ electrodes were prepared by electrodeposition in laboratory-scale Swagelok® T-cells with three-electrode configuration by using a VSP potentiostat/galvanostat (Bio-Logic). In all electrodeposition experiments, platinum wire (Goodfellow GmbH, 99.99%, $\varnothing=0.8 \text{ mm}$) was used as the CE and pseudo-RE and the particular nickel substrate as the WE. MnO₂ bulk foil electrodes were prepared by using nickel foil (Carl Schlenk AG, $\geq 99.9\%$, $\varnothing=12 \text{ mm}$, 50 μm thick) as a substrate for MnO₂ deposition, whereas MnO₂ foam electrodes were achieved by using nickel foams as the host matrix. Prior to all electrodeposition experiments, the platinum electrodes were polished with polycrystalline diamond solutions (grain size: 1–15 μm , Buehler) and rinsed with water to remove surface contaminations. Electrodeposition was performed by using a freshly prepared aqueous electrolyte solution containing 0.1 M MnSO₄·H₂O ($\geq 99\%$), 0.1 M Na₂SO₄ ($\geq 99\%$), and 0.1 M CH₃COONa ($\geq 99\%$). Cathodic pulses (1.8 V versus Pt, 0.2 s on and 10 s off) were applied to the nickel substrates for varying plating times (nickel foam: 1, 3, 6, or 7 h; nickel foil: 96 h).^[43] Afterwards, the cells were disassembled and as-prepared MnO₂ electrodes were rinsed with double-distilled water to remove redundant electrolyte and, subsequently, the electrodes were dried in a glass oven (Büchi Labortechnik GmbH) at 100 °C overnight under reduced pressure.

Structural and morphological characterization of the MnO₂ electrodes

SEM was used to investigate the topography and morphology of the polymer template, nickel foam, and MnO₂ electrodes prepared with different deposition times. The micrographs were recorded with an Auriga CrossBeam workstation from Zeiss with

a field-emission gun (Schottky-type) at an acceleration voltage of 3 kV and a working distance of 2.0 mm by using the InLens detector. Prior to SEM imaging, the polymer template was sputter-coated with gold (ChemPUR GmbH, 99.99%) for 30 s at 5 mA (Quorum Technologies Q150T).

For structural and morphological investigations of the MnO₂ deposit, a Raman spectrum of a reference bulk deposit on nickel foil was recorded by using a Bruker SENTERRA dispersive Raman microscope equipped with a green frequency doubled Nd:YAG laser with a wavelength of 532 nm. Thus, the laser power and spectral resolution were adjusted to 5 mW and 3–5 cm^{-1} , respectively. The integration time was set to 60 s and 30 scans were recorded.

XRD measurements of the deposit were performed by using a Bruker D8 Advance X-ray diffractometer with a copper target X-ray tube in the range $2\theta=20$ to 90° with a step size of 0.01° per 1.5 s (200 min per XRD scan) and at an accelerating voltage and current flow of 40 kV and 30 mA, respectively.

The porosity of the prepared MnO₂ electrodes was determined by using ImageJ 1.50j software.^[37]

Electrochemical characterization of MnO₂ electrodes

Electrochemical investigations of the prepared nanostructured MnO₂ electrodes and the reference bulk MnO₂ electrode were performed in laboratory-scale Swagelok® T-cells with a three-electrode arrangement by using metallic lithium foil (Rockwood Lithium, 99.99%) as the CE ($\varnothing=12 \text{ mm}$) and RE ($\varnothing=6 \text{ mm}$) on a VSP potentiostat/galvanostat (Bio-Logic). An electrolyte formulation composed of 1 M LiPF₆ (battery grade) in EC/DMC 1:1 (w/w ; BASF, battery grade) and a nonwoven separator (Freudenberger®FS2190) were used. The cells were assembled in an argon-filled glove box (MBraun) with an atmospheric water and oxygen content below 0.1 ppm. For every investigation, three MnO₂ electrodes obtained after a defined deposition time were prepared and investigated.

Electrochemical investigations of the MnO₂ electrodes encompassed three steps: cyclic voltammetry experiments, followed by a cell capacity determination (CCD) step, and finally galvanostatic cycling experiments. Cyclic voltammograms of the MnO₂ electrodes were recorded in the potential range from 0.01 to 2 V versus Li/Li⁺ at a scan rate of 1 mVs^{−1} for 3 cycles. To determine the maximum actual capacity, C , of the distinct MnO₂ electrodes, a current of 40 μA was applied in a prelithiation/delithiation cycle. Based on the determined value of C , the desired current, I , was calculated for subsequent galvanostatic cycling of the electrodes. First, the cells were cycled with 1 I (30 cycles), followed by cycling with 2 (3), 5 (3), and 10 I (5 cycles), to validate the C-rate capability of the electrodes. Afterwards, the cells were cycled with 1 I for an additional 35 or 155 cycles. Galvanostatic cycling of the MnO₂ electrodes was performed in the potential range from 0.01 to 2 V versus Li/Li⁺.

Acknowledgements

Financial support from the Federal Ministry of Education and Research (BMBF) within the project “Electrolyte-Labor 4e” (project number 03X4632) is gratefully acknowledged. Fur-

thermore, we would like to thank Matthias Eilers-Rethwisch for performing the XRD measurements.

Keywords: electrochemistry • lithium • polymers • surface chemistry • templated synthesis

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Received: July 27, 2016

Revised: September 24, 2016

Published online on November 25, 2016