Nanoconfined NaAlH₄ Conversion Electrodes for Li Batteries

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Abstract: In the past, sodium alanate, NaAlH₄, has been widely investigated for its capability to store hydrogen, and its potential for improving storage properties through nanoconfinement in carbon scaffolds has been extensively studied. NaAlH₄ has recently been considered for Li-ion storage as a conversion-type anode in Li-ion batteries. Here, NaAlH₄ nanoconfined in carbon scaffolds as an anode material for Li-ion batteries is reported for the first time. Nanoconfined NaAlH₄ was prepared by melt infiltration into mesoporous carbon scaffolds. In the first cycle, the electrochemical reversibility of nanoconfined NaAlH₄ was improved from around 30 to 70% compared to that of nonconfined NaAlH₄. Cyclic voltammetry revealed that nanoconfinement alters the conversion pathway, and operando powder X-ray diffraction showed that the conversion from NaAlH₄ into Na₃AlH₆ is favored over the formation of LiNa₂AlH₆. The electrochemical reactivity of the carbon scaffolds has also been investigated to study their contribution to the overall capacity of the electrodes.

Introduction

Conversion-type electrodes are interesting alternatives to conventional intercalation electrodes for Li-ion batteries mainly due to their high capacities. In conversion-type electrodes, lithium reacts with the electrode material through a simple reaction that is generally described as follows: \( M \cdot X_n + (b - n) Li \leftrightarrow aM + bLi \cdot X \), where \( M \) is a transition metal, \( X \) is an anion, and \( n \) is the oxidation state of \( X \). However, this class of electrodes is still far from reaching commercial applications, as the electrodes suffer from large voltage hysteresis between the discharge and charge reactions, poor Coulombic efficiency in the first cycle; and, in many cases, poor cycling performance due to structural reorganization, particle decohesion, and phase separation.¹ Hence, design and investigation of novel conversion-type electrode materials is needed to develop upon this class of materials.

Metal hydride materials, which have previously been investigated as hydrogen storage materials for energy purposes,² are now receiving increased attention as a new class of electrode materials.³ Light-element hydrides possess higher gravimetric and volumetric energy densities than those of any known conversion-type material. The properties of magnesium hydride, MgH₂, as an electrode were first investigated by Oumellal and co-workers, and it was shown to have a high reversible capacity of 1480 mAh/g and small voltage hysteresis of ~0.2 V.⁴ The use of a metal hydride as a negative electrode of rechargeable batteries is not limited to binary metal hydride systems; complex transition metal hydrides, Mg₄MH₆ (M = Fe, Co, Ni),⁵ and lightweight alkaline alanates have also been considered.⁶⁻⁸

Sodium alanate, NaAlH₄, has a theoretical gravimetric capacity of 1985 mAh/g. A two-step conversion lithiation reaction of NaAlH₄ is described by Latroche and co-workers, as follows:

\[
\begin{align*}
NaAlH_4 + 3/2Li & \rightarrow 1/2LiNa_2AlH_6 + 1/2Al + LiH \\
LiNa_2AlH_6 + 5Li & \rightarrow 2Na + Al + 6LiH
\end{align*}
\]

(1)

(2)

The complete conversion reaction involves the exchange of four Li ions through the formation of the intermediate LiNa₂AlH₆. This reaction pathway is based on observations made by powder X-ray diffraction. Subsequently, Reale and co-workers proposed the existence of a second conversion path via Na₃AlH₆ through observations made by in situ powder X-ray diffraction through the following reaction:

\[
NaAlH_4 + 2Li \rightarrow 1/3Na_3AlH_6 + 2/3Al + 2LiH
\]

(3)

The possible coexistence of two intermediates makes the electrochemical conversion of NaAlH₄ more complicated.
system than typical hydride systems. However, similar to other conversion-type electrodes, NaAlH₄ also suffers from poor reversibility, which may be attributed to the large volume change and phase separation during electrochemical operation. This calls for new approaches to improve the performance of metal hydrides as conversion-type electrodes.

Nanoconfinement is a bottom-up approach wherein a material is infiltrated into a chemically inert nanoporous scaffold. This approach effectively limits the particle size to the size of the pores and cavities in the scaffold and may also reduce phase separation during chemical conversion.9,10 Nanoporous carbon aerogels with varying pore sizes and volumes are often used as the confining scaffolds, and a wide range of different metal hydrides have been nanoconfined, with a focus on hydrogen storage properties, for example, MgH₂, NaAlH₄, and reactive hydride composites, 2LiBH₄–MgH₂.9,11–14 There is a strong kinetic effect for hydrogen release and uptake and a smaller “nanoeffect” for pore sizes (D) < ~30 nm.15 One advantage of carbon aerogel scaffolds is that the surface area and pore volume can be increased by a postsynthetic treatment (heating to >600 °C in CO₂), typically referred to as activation, while maintaining a relatively constant pore size.16,17 Thus, relatively large amounts of active metal hydride material can be infiltrated to reach large energy densities, with potential for use in both batteries and hydrogen storage. Compared to those in nonactivated carbon aerogel, NaAlH₄ in activated-carbon aerogel shows slower kinetics but a more stable hydrogen storage capacity upon cycling.16 The carbon aerogels are electronically conductive and also function as an effective current collector for the electrode as an intimate contact to the conversion-type metal hydride is maintained. This property is similar to that of metallic sponges, for example, Ni sponges, which are often employed in electrode fabrication.18 Moreover, the small particle size of the confined electrode material and the high surface area reduce the diffusion distances of Li ions and improve the reactivity. Nanoconfinement in mesoporous carbon has been used for improving the performances of conversion electrodes such as FeF₂ and P.5,19,20 It has been reported that MgH₂ nanoconfined in porous carbon (surface area, S BET = 500 m²/g) after ball milling demonstrates good cyclic stability.21 These results encourage further studies for enhancing the properties of light-element metal hydride electrodes by nanoconfinement, which is the focus of the present investigations.

In this article, we report on the electrochemical performance of NaAlH₄ nanoconfined by melt infiltration in two types of conductive mesoporous carbon scaffolds that have previously been investigated in rechargeable batteries: resorcinol formaldehyde carbon aerogel22–25 and CMK-3.24–26 We show through cyclic voltammetry (CV) and operando synchrotron radiation powder X-ray diffraction (SR-PXD) that nanoconfinement alters the reaction mechanism of the lithiation process.

## RESULTS AND DISCUSSION

To study the effect of nanoconfinement in different mesoporous carbon scaffolds on the electrochemical reactivity of NaAlH₄ electrode samples of NaAlH₄ melt-infiltrated into a resorcinol formaldehyde carbon scaffold (Na_CA) and into a mesoporous carbon CMK-3 (Na_CMK3) as well as a sample of ball-milled NaAlH₄ (Na_BM) were prepared (see Table 1). Carbon aerogel and CMK-3 were prepared by pyrolysis at a high temperature (2800 °C), followed by further heat treatment. This treatment eliminates hydrogen and oxygen in the carbon scaffolds27,28 and thereby eliminates possible reactions between the scaffold and NaAlH₄ during melt infiltration. Furthermore, it is reported that carbon materials demonstrate large voltage hysteresis, and the extent of hysteresis is proportional to the hydrogen content.29 Thus, removal of the H-group helps reduce hysteresis by minimizing the quasi-reversible binding between Li and the hydrogen-terminated edges of the scaffold.28

Before infiltration, both CA and CMK-3 have surface areas of above 1000 m²/g. CMK-3 has a uniform pore size of 4.7 nm, whereas CA has a broader pore size distribution, with an average diameter of 24.3 nm (see Supporting Information Figure S1). After infiltration, both the surface area and total pore volume of the carbons, as determined by N₂ adsorption measurements, decrease dramatically (see Table 2). Both CA and CMK-3 comprise fully accessible and highly interconnected pore networks. In such open pore spaces, percolative blocking (e.g., due to pore mouth blocking) is highly unlikely, especially for nitrogen molecules. In this respect, the decrease in the amount adsorbed (and thus the deduced pore volume) is a very strong indication of successful NaAlH₄ infiltration.

In the case of the CA scaffold, NaAlH₄ infiltration leads to an almost 80% reduction in the initial total pore volume (from 2.04 to 0.38 cm³/g), in good agreement with the theoretical vol % hydride loading (as calculated based on the actual amount of NaAlH₄ used for the infiltration and its bulk density). For Na_CMK3, the total pore volume decreases from 1.20 to 0.80 cm³/g, which corresponds to a filled pore volume of 33%, lower than the theoretical loading of 46 vol %. This deviation suggests that in the case of CMK-3 a small quantity of NaAlH₄ might also reside on the external surface of the carbon particles, without, however, affecting the accessibility of the pores. Complete pore mouth blocking or infiltration failure should be ruled out, as the former would lead to zero N₂ adsorption and the latter, to no pore volume reduction for the NaAlH₄/CMK-3 composite.

High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) coupled with energy

| Table 1. Investigated Samples and Preparation Methods |
|------------------------------|------------------------------|------------------------------|
| Sample | Sample Name | Treatment |
| NaAlH₄ | Na_BM | bulk, ball milled for 2 h |
| NaAlH₄ | Na_CA | NaAlH₄ melt-infiltrated in activated-carbon aerogel |
| NaAlH₄ | Na_CMK3 | NaAlH₄ melt-infiltrated in heat-treated CMK-3 |
| Carbon aerogel | CA | activated in CO₂ flow for 5 h at 950 °C |
| CMK-3 | CMK-3 | heat-treated in Ar flow at 700 °C |

| Table 2. Morphological Parameters of Empty and Infiltrated Carbon Scaffolds |
|------------------------------|------------------------------|------------------------------|
| Sample | Surface Area S BET (m²/g) | Average Pore Size D max (nm) | Total Pore Volume V tot (cm³/g) | NaAlH₄ (wt %)¹ | NaAlH₄ (vol %)² |
| CA | 1586 | 24.3 | 2.04 |
| Na_CA | 78 | 21.9 | 0.38 | 69 | 79 |
| CMK-3 | 1162 | 4.7 | 1.20 |
| Na_CMK3 | 772 | 3.7 | 0.80 | 40 | 46 |

¹Calculation based on the quantity of NaAlH₄ being added for melt infiltration. ²Calculated from the bulk density of NaAlH₄ and the total pore volume of the scaffold.
dispersive X-ray (EDX) elemental mapping of a CA scaffold particle containing NaAlH₄ shows that NaAlH₄ is dispersed in the CA scaffold and no significant agglomeration is observed (see Figure 1). For Na_BM, particles >150 nm in diameter were obtained by ball milling (see Supporting Information Figure S2). We note that high-resolution TEM was attempted, but the high-energy electron beam unfortunately caused the hydride to decompose. The EDX spectrum of Na_BM confirms the absence of impurities from the milling jars. Also, for Na_CA, no impurities were observed.

The PXD patterns of the as-prepared samples are shown in Figure 2a. After ball milling of the as-received NaAlH₄ (Na_BM), only diffraction from NaAlH₄ was observed, whereas in both nanoconfined samples (Na_CA and Na_CMK3) a small amount of Al was observed due to partial decomposition of NaAlH₄ during infiltration. The amount of Al in Na_CA is 3.45 wt % on the basis of Rietveld refinement. It has been reported that nanoconfined NaAlH₄ upon partial decomposition decomposes into NaH and Al directly. Thus, the presence of the intermediate Na₃AlH₆ in Na_CMK3 suggests that some of the NaAlH₄ is not confined inside pores. Moreover, because the pore size of CMK-3 is 4.7 nm, the Bragg peaks of infiltrated NaAlH₄ would not be easily observable by PXD due to extensive peak broadening. Hence, the sharp diffraction peaks from NaAlH₄ in Na_CMK3 likely originate from noninfiltrated NaAlH₄. In contrast, an increase in the full width at half-maximum (FWHM) (without instrumental correction) is evident in the PXD data of Na_CA after nanoconfinement; for example, it increases from 0.075° in Na_BM to 0.107° in Na_CA for the (112) peak at 2θ = 29.6°. However, for a crystallite size of 24 nm (the average pore size), the expected FWHM (without instrumental correction) is ~0.34°. The observed FWHM corresponds to a particle size of 102 nm (corrected for instrumental broadening). Hence, by PXD, we mainly observe NaAlH₄ which is not infiltrated into the scaffold. However, it still confirms that besides Al no crystalline impurities are observed. Moreover, it is evident that the particle size of even the surface NaAlH₄ is reduced compared to that in the ball-milled sample, Na_BM. For the nanoconfined samples, the presence of amorphous scaffolds is observed as contributions to the background signal below 2θ ~ 35°.

**Galvanostatic Test and PXD of NaAlH₄ Electrodes.** In Table 3, the possible lithiation reactions of NaAlH₄ are listed, with their calculated potentials, E(calc) versus those of Li, as reported in previous publications. By Nernst’s law ΔG = −nFE(eq (where ΔG is the Gibbs free energy of the reaction, n is the number of electrons, and F is the Faraday constant); a higher equilibrium potential indicates a more negative ΔG, that is, a thermodynamically more favorable reaction. In the first galvanostatic discharge (see Figure 3), all samples exceeded the theoretical capacity (equivalent to four Li ions). The capacity observed at around 0.75–0.82 V versus Li is likely related to the formation of a solid electrolyte interface (SEI). It is also known that formation of LiAl alloy may occur at a low potential (0.29–0.36 V vs Li, see Table 3). The formation of SEI and LiAl alloy contribute to the extra capacity of NaAlH₄ electrodes. The experimental potentials are generally lower than the predicted values, likely due to kinetic limitation. Moreover, thermodynamic overpotential is neglected for the estimation of potentials in the literature. For Na_BM, the potential is relatively constant in between x = 0.3 and 2.2 Li equivalents. From Table 3 it is observed that conversion from NaAlH₄ to LiNa₂AlH₆ (reaction 1) is slightly
more thermodynamically favorable than conversion to Na3AlH6 (reaction 3). Hence, the flat plateau of Na_BM should correspond to reaction 1. Ex situ PXD of Na_BM after the first discharge confirms that reaction 1 as well as reactions 2 and 5 take place, as diffraction peaks from LiNa2AlH6, Na, Al, and LiAl are observed. LiH is not observable because of the small scattering factor. There is no sign of formation of Na3AlH6; thus, reaction 3 does not occur in the nonconfined sample or occurs to a much smaller extent than in the nanoconfined sample. This is in accordance with the observation made by Latroche et al.6

In contrast to that for Na_BM, the voltage curve for Na_CA shows a more gradual slope from x = 0.48 to 2.0 Li equivalents in the first discharge. For Na_CA, ex situ PXD indicates that both reactions 1 and 3 occur (see Figure 4a), as weak reflection from Na3AlH6 is observed along reflections from LiNa2AlH6, Na, Al, and LiAl. Again, LiH is not observable because of the small scattering factor. The potentials of reactions 1 and 3 are very close (a difference of only 0.03 V), and these reactions may occur in parallel. Galvanostatic intermittent titrations during discharge and charge of the Na_BM and Na_CA samples (Figure 3b,c) result in relatively large voltage relaxations during 15 h under open circuit voltage conditions. For Na_BM the relaxations are in the range of 0.17−1.87 V, whereas for Na_CA, they range from 56 to 533 mV. This indicates that a large fraction of the high-voltage hysteresis between charge and discharge is due to kinetic limitations of the material. This even seems to be more severe in the ball-milled material compared with the nanoconfined material. For Na_CA, wherein around 50% recharge is achieved, a potential of 0.69 V is observed at x Li = 2.75 after relaxation, whereas during discharge, a potential of 0.43 is observed at 2.4 Li equivalents. This voltage hysteresis can be ascribed to factors affecting the thermodynamics, such as structural changes.

After the first discharge, small peaks of NaAlH4 are found in both Na_BM and Na_CA, suggesting that the conversion is not fully complete. However conversion of NaAlH4 to LiNa2AlH6 and then to metallic Na and Al is confirmed as is the formation of the LiAl alloy, which is also observed in both samples. Na3AlH6 is only observed during the discharge of the nanoconfined sample, Na_CA.

For Na_CMK3, the discharge−charge curve is significantly different, for example, the plateau at 0.45 V versus Li is significantly shorter than that for the other samples, and even though Na_CMK3 has a high capacity, only a small fraction seems to originate from the desired conversion reaction of NaAlH4. As seen in Figure 4a, mainly the LiAl alloy is formed during the first discharge of Na_CMK3. The Bragg peaks at 2θ < 23° could be related to reactions between the material and electrolyte. Upon cycling, the discharge−charge curve of Na_CMK3 (not shown) becomes more similar to that of empty CMK-3, as reported in the literature, which shows a large hysteresis without any plateau in the charge cycle.33 Because Na_CMK3 is not very reactive, we focus only on Na_BM and Na_CA in the following diffraction analysis.
Na_CA performs better than Na_BM in the first charge. The initial columbic efficiencies of Na_CA and Na_BM were around 70 and 30%, respectively. Both samples had a plateau at 0.43 V versus Li, which is believed to be attributed to the

| reaction | Ecalc (V vs Li) | references |
|----------|----------------|-------------|
| NaAlH4 + 3/2Li = 1/2Li2NaAlH6 + 1/2Al + LiH | 0.73−0.76 | refs 6 and 7 |
| LiNa2AlH6 + 3Li = 2Na + Al + 6LiH | 0.54−0.56 | refs 6 and 7 |
| NaAlH4 + 2Li = 1/3Na3AlH6 + 2/3Al + 2LiH | 0.70−0.72<sup>b</sup> | ref 7 |
| NaAlH4 + 6Li = 3Na + Al + 6LiH | 0.52<sup>c</sup>−0.53 | ref 7 |
| Li + Al = LiAl | 0.29−0.36 | refs 6 and 8 |

<sup>a</sup>Note: values for reactions 3 and 4 (marked by “b”) are also calculated herein. <sup>b</sup>Calculated from the reported Gibbs free energy of formation of the compounds<sup>31</sup> (taking reaction 3, NaAlH4 + 2Li = 1/3Na3AlH6 + 2/3Al + 2LiH, as an example, the ΔG of the reaction is equals to 1/3ΔG(Na3AlH6) + 2ΔG(LiH) − ΔG(NaAlH4) = 1/3(−116.23) + 2(−69.96) − (−39.43) = −139 kJ/mol) and converted to the potential by ΔG = −nFE<sub>eq</sub>.
According to the galvanostatic charge data, neither of the Al observed at 0.43 V versus Li in the galvanostatic test. The observation of Na in the pretreatment is supported by the PXD pattern of recharged Na_CA (see Figure 4b). The reformation of the intermediates and NaAlH₄. This interpretation is supported by the PXD pattern of recharged Na_CA during the charge cycle. Hence, the peaks observed in Na_CA acts differently within the same potential range. More peaks are observed from 0.65 to 1.8 V versus Li in the reverse scan, meaning more reactions take place (see Figure 5b). In contrast to Na_BM, Na_CA has a broad peak at a potential below 0.5 V versus Li, which is also observed in the voltammogram of empty CA (see Figure 5c). Intercalation of Li into carbon can happen at a low potential close to 0 V versus Li. Therefore, the broadening of the peak may correspond to the intercalation of Li into CA. When CA was scanned from 0.005 to 3.0 V versus Li, very limited current response was observed, and no significant reactions take place during the charge cycle. Hence, the peaks observed in Na_CA are solely related to the reactivity of NaAlH₄ and its intermediates. In the second cycle, only three broad peaks remain, suggesting poor to no reversibility of these reactions in Na_CA. In the fifth cycle, the only remaining peak at 0.5 V corresponds to the intercalation of Li into CA. When CA was scanned from 0.005 to 3.0 V versus Li, very limited current response was observed, and no significant reactions take place during the charge cycle. Hence, the peaks observed in Na_CA are solely related to the reactivity of NaAlH₄ and its intermediates. In the second cycle, only three broad peaks remain, suggesting poor to no reversibility of these reactions in Na_CA. In the fifth cycle, the only remaining peak at 0.5 V corresponds to the intercalation of Li into CA. When CA was scanned from 0.005 to 3.0 V versus Li, very limited current response was observed, and no significant reactions take place during the charge cycle. Hence, the peaks observed in Na_CA are solely related to the reactivity of NaAlH₄ and its intermediates. In the second cycle, only three broad peaks remain, suggesting poor to no reversibility of these reactions in Na_CA. In the fifth cycle, the only remaining peak at 0.5 V corresponds to the intercalation of Li into CA.
observed in Na_CA. There is another small peak at 0.89 V versus Li in Na_CMK3, but it is not reversible.

From the CV results of infiltrated and empty carbon scaffolds, it is found that the reactivity of nanoconfinned NaAlH4 is not a simple sum of the data measured separately for nonconfinned NaAlH4 and the empty carbon scaffold. Nano-confinement changes the reaction mechanism. However, the peaks in the voltammograms are heavily overlapped and it is difficult to distinguish each reaction step. To acquire more information on the reaction mechanism, the samples were investigated by operando SR-PXD.

Operando SR-PXD Studies. Figure 6 shows the operando SR-PXD data of Na_BM and Na_CA stacked as a function of Li uptake, x. As the conversion of NaAlH4 is not complete in the operando SR-PXD study (for both samples, less than 2.4 Li equivalents was exchanged), we focus on the qualitative information, as the data provide very useful information for understanding the effect of nanoconfinement and the presence of the carbon scaffold on NaAlH4. The lower capacity observed in these experiments is due to the higher internal resistance of the operando cell compared to that of a normal coin cell, resulting in a larger overpotential and the lower potential limit being reached at a lower state of discharge, that is, at lower x(Li)-values.

Before discharging (at x(Li) = 0.0), both samples contain Al, which is either from partial decomposition of NaAlH4 or the Al-foil current collector in the operando battery cell. For Na_BM, the conversion of NaAlH4 to LiNa2AlH6 is initiated at x(Li) = 0.27, as expected. The intensity of LiNa2AlH6 increases continuously up to x(Li) = 1.43. A fraction of the LiNa2AlH6 may decompose into Na, Al, and LiH with time, as demonstrated by the slightly decreasing intensity of LiNa2AlH6 as well as the increasing intensity of Na and Al. In contrast to the ex situ PXD result, Na3AlH6 also forms in Na_BM. The formation of Na3AlH6 initiates at a deeper discharge state of x(Li) = 1.07. This result is consistent with the reaction...
mechanism proposed by Reale et al.7 As mentioned previously, the conversion from NaAlH4 to Na3AlH6 is less favorable and a smaller amount of Na3AlH6 is formed compared to that of LiNa2AlH6. The small amount of Na3AlH6 and poor resolution of the ex situ PXD pattern may explain why Na3AlH6 is not found in the ex situ PXD pattern (Figure 4a).

For Na_CA, the first conversion step is again the conversion to LiNa2AlH6 occurring at x(Li) = 0.57. Shortly after the formation of LiNa2AlH6, the formation of Na3AlH6 is also initiated, at x(Li) = 0.63. Hence, the use of the carbon scaffold seems to favor the conversion to Na3AlH6 which is in accordance with the observations made by ex situ PXD. Compared to that in Na_BM, there is less LiNa2AlH6 present in Na_CA. As shown in Figure 6b, conversion to LiNa2AlH6 and Na3AlH6 occurs in parallel. This indicates that the conversions to LiNa2AlH6 and Na3AlH6 are competing reactions. It is believed that alteration of the reaction mechanism is most probably due to a kinetic factor because thermodynamic effects are only expected when the particle size is smaller than 2–3 nm.30

Cycling Stability. In the ex situ PXD of Na_BM and Na_CA after 20 discharge–charge cycles, mainly Na, Al, and the LiAl alloy are present (see Figure 7). The PXD patterns indicate that conversion to NaAlH4 or any intermediate

Figure 5. Cyclic voltammograms of (a) Na_BM, (b) Na_CA, (c) CA, (d) Na_CMK3, and (e) CMK-3 at a scan rate of 0.1 mV/s.
becomes difficult after repeated cycles. The capacities (mA h/g of NaAlH₄) of the three NaAlH₄ samples in the first 20 cycles are plotted in Figure 8a. Generally, all samples show a significant fall in capacity between the first and second cycles. One of the reasons of the rapid decrease in capacity is due to the formation of SEI. However, nanoconfinement in the carbon scaffold increases the capacity retention from around 23% (Na_BM) to 43% (Na_CA) and 46% (Na_CMK3). After 20 discharge–charge cycles, Na_CMK3 has the highest capacity, while Na_BM has the lowest capacity.

From the previous sections, it is evident that the reversibility of NaAlH₄ diminishes gradually. As the carbon scaffolds are found to be electrochemically active, it is important to access their contribution toward the overall capacity of the electrodes.

Electrodes of Na_CA and CA containing the same amount of carbon scaffold (0.9 mg) were tested by galvanostatic discharge–charge cycling. Na_CA was cycled at a rate of C/10 on the basis of the amount of NaAlH₄ and the same current was applied to CA. Na_CA has a higher capacity than that of CA during the first five cycles, whereas the opposite is observed for the subsequent cycles (see Figure 8b). The higher capacity of Na_CA during the initial five cycles is due to the reactivity of NaAlH₄.

After 20 cycles, CA has a capacity of 0.70 mA h, which is equal to 773 mA h/g CA with a Coulombic efficiency of 95.6%. Interestingly, although the Coulombic efficiency is not very high, the capacity of CA is significantly higher than the capacity of graphite (372 mA h/g). Na_CMK3 was also compared with CMK-3. The capacity of CMK-3 is higher than that of Na_CMK3 in all cycles, and it retains 548 mA h/g of CMK-3 after 20 cycles. From Figures 8b,c, it is clear that carbon scaffolds contribute to the overall reversible capacity, as is also revealed from the results of CV.

**CONCLUSIONS**

We have presented the electrochemical performance and electrochemically driven conversion mechanism of the NaAlH₄ anode nanoconfined in mesoporous carbon scaffolds. The initial Coulombic efficiency of NaAlH₄ confined in activated-carbon aerogel is at least twice that of ball-milled NaAlH₄. Using the activated-carbon aerogel also improves the kinetics of the conversion from NaAlH₄ to Na₂AlH₆ and thereby seems to alter the conversion mechanism. However, it has been found that the capacity of nanoconfined NaAlH₄ is initially dominated by the reactivity of the NaAlH₄ and LiAl alloys but later by the carbon scaffold. The loss in the reactivity of NaAlH₄ could be related to inefficient diffusion of the hydride, which may limit the extent of hydride conversion.

Nanoconfinement is a promising route for improving hydride electrodes; however, research on nanoconfinement is still at a preliminary stage and many aspects have to be considered. To enhance the reactivity of nanoconfined hydride, it is important to maximize the loading of hydride inside the scaffold, which will also increase the material capacity. It is also interesting to study the influence of pore size and different activation methods on the electrochemical reactivity of the carbon scaffold. A smaller pore size of the scaffold is expected to enhance the kinetics of the material and may also reduce polarization of the electrode. New electrically conductive but inert scaffolds may also need to be explored to understand the nanoconfinement effect in more detail.
METHODS
Apart from the synthesis of the carbon scaffolds (resorcinol formaldehyde carbon aerogel and CMK-3), all sample preparations and handling were carried out in an argon-filled glovebox equipped with a circulation purification system. The O$_2$ and H$_2$O levels were below 1 ppm at all times.

Synthesis of Carbon Aerogel. Resorcinol formaldehyde carbon aerogel was prepared by mixing resorcinol (≥99.0%; Sigma-Aldrich), formaldehyde (37 wt % in H$_2$O, stabilized by 10–15% methanol; Sigma-Aldrich), and Na$_2$CO$_3$ (99.999%; Aldrich) in deionized water. The molar ratio was 1:2:8:0.0008 resorcinol/formaldehyde/H$_2$O/Na$_2$CO$_3$. In general, for the synthesis of the scaffold, the procedures described in refs 11 and 39 were used. Herein, the mixture was aged at RT for 24 h, at 50 °C for 24 h, and at 90 °C for 72 h. After cooling, the carbon aerogel was soaked in excess acetone. Finally, the carbon aerogel was pyrolysed at 800 °C ($\Delta T/\Delta t = 3$ °C/min) under N$_2$ flow for 6 h. The surface area and total pore volume of the carbon aerogel was increased by heating the aerogel to 950 °C ($\Delta T/\Delta t = 6$ °C/min) in a constant CO$_2$ flow for 5 h according to the procedure described in ref 17. This procedure denoted activation of the resorcinol formaldehyde carbon scaffold, and henceforth, this scaffold is denoted as CA. The increased surface area and total pore volume would enhance the infiltration of NaAlH$_4$.

Synthesis of CMK-3. The CMK-3-type carbon scaffold was synthesized using a well-established nanocasting route, as described in ref 40, using SBA-15, a two-dimensional hexagonally ordered mesoporous silica, as the template. The SBA-15 template was also prepared for this purpose by adopting a standard surfactant-templating method, as described in ref 41. The synthesized SBA-15 silica template was infiltrated with a solution of sucrose and sulfuric acid, carbonized by pyrolysis up to 900 °C under N$_2$ flow, and finally washed with HF at RT to remove the silica. The as-prepared CMK-3 mesoporous carbon was further heat-treated in a tubular furnace up to 700 °C under Ar flow to remove any residual oxygen-containing groups produced on the carbon surface during the synthetic steps. The sample obtained by this thermal treatment is denoted as CMK-3.

Preparation of Nanoconfinned and Ball-Milled NaAlH$_4$. Prior to melt infiltration, the carbon scaffolds, CA and CMK-3, were degassed in vacuum at 350 °C for several hours. For melt infiltration, NaAlH$_4$ (93%; Aldrich) and the degassed scaffold were added to a Swagelok-type autoclave inside an Ar-filled glovebox. To avoid decomposition of NaAlH$_4$ melt infiltration was performed at $p$(H$_2$) = 210–230 bar. The mixture was heated to 195 °C ($\Delta T/\Delta t = 2$ °C/min) and dwelled for 15 min; it was then cooled to RT. These samples are denoted as Na_CA and Na_CMK3.

Figure 8. (a) Specific capacity of the sodium alanate samples at rate C/10 relative to the mass of NaAlH$_4$ (mA h/g of NaAlH$_4$). (b) Capacity of Na_CA vs that of empty CA under the same applied current. (c) Capacity of Na_CMK3 versus that of empty CMK-3 under the same applied current. Insets: Coulombic efficiency of the corresponding measurements.
The reactivity of as-received NaAlH₄ was improved by ball milling for 2 h (5 min milling, 2 min pause, and 24 repetitions) using a Fritsch Pulverisette No. 6 with a speed of 350 rpm. The milling was performed in an 80 mL tungsten carbide (WC) vial using 10 mm WC balls and a ball-to-powder mass ratio of approximately 30:1. This sample of NaAlH₄ is denoted as Na_BM.

**Surface Area and Pore Size Determination.** The pore properties of the CA and CMK-3 scaffolds and composites before and after melt infiltration of NaAlH₄ were deduced from N₂ adsorption/desorption measurements at 77 K using a Nova 2200e surface area and pore size analyzer (Quantachrome Instruments). The surface area (S BET) was determined by the Brunauer–Emmett–Teller (BET) method, whereas the mean pore size (D mean) was obtained from the desorption isotherm by the Barrett–Joyner–Halenda method. The total pore volume (V tot) was calculated from the amount of N₂ adsorbed at p/p0 = 0.98 (by assuming an adsorbate density of 0.807 g/cm³).

**EDX Spectroscopy.** The composition of the prepared samples, Na_BM and Na_CA, was characterized using an FEI Talos F200X scanning/transmission electron microscope with a HAADF detector and EDX system. Powders of the samples were added to anhydrous cyclohexane (99.5%; Sigma-Aldrich) and a few drops of the suspension were spread onto the copper grid. The sample grids were placed on a sample holder and transferred into the chamber in air; hence, the samples were oxidized partially prior to measurements.

**Electrochemical Test.** Coin cells (CR2032) were assembled in an Ar-filled glovebox. The working electrodes were prepared by thoroughly grinding the samples with acetylene black (Cabot Corporation) and carboxymethyl cellulose (CMC) (SAFT) powders in a 3:1:1 mass ratio. The sample grids were placed on a sample holder and mounted in the cells in an Ar-filled glovebox using Whatman borosilicate glass-ber separator (Whatman GF/B) with 1 M LiPF₆ in 1:1 EC/DMC as the liquid electrolyte. A piece of aluminum foil (thickness ~0.011 mm) was placed behind the working electrode to ensure uniform conductivity. The operando SR-PXD data were collected at beamline I711, MAXII in Lund, Sweden, using a selected wavelength of λ = 0.9940 Å. Diffraction patterns were collected in transmission geometry every 10 min with 45 s of exposure time using a large-area CCD detector. During collection of the SR-PXD data, the cell was galvanostatically discharged using a current rate of C/20 and a cutoff potential of 0.005 V versus Li.

The collected diffraction patterns were integrated using the Fit2D software. Rietveld refinement of selected diffraction patterns was performed using Fullprof suite software. The shape of the diffraction peaks was described by the pseudo-Voigt profile function, whereas the background was refined using linear interpolation between selected points.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00143.

Pore size distributions of the carbon scaffolds (CA and CMK-3); HAADF-STEM images and EDX elemental mapping of the ball-milled NaAlH₄ sample (Na_BM); EDX elemental mapping of nanoconfined NaAlH₄ (Na_CA) (PDF)

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**Notes**

The authors declare no competing financial interest.

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