Homogeneous guiding deposition of sodium through main group II metals toward dendrite-free sodium anodes

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Metallic sodium is a potential anode material for rechargeable sodium-based batteries because of its high specific capacity and low cost. However, sodium commonly suffers from severe sodium dendrites and infinitely huge volume change, hampering its practical applications. Here, we demonstrate that sodium can be controllably deposited through main group II metals such as Be, Mg, and Ba since they have definite solubility in sodium and thus enable a marked reduction of the nucleation barriers of sodium, guiding the parallel growth of sodium on the metal substrates. By further homogeneously dispersing Mg clusters in a three-dimensional hierarchical structure on the basis of a carbonized Mg-based metal-organic framework–74 membrane, the nucleation barriers of sodium can be eliminated, owing to the plentiful Mg nucleation seeds. Hence, a dendrite-free sodium metal anode with a very low overpotential of 27 mV and a superior cycling stability of up to 1350 hours is achieved.

INTRODUCTION

Sodium (Na)–based batteries, including sodium metal, sodium-sulfur, and sodium-air batteries, have been considered as potential candidates for power grids and electric vehicles, owing to the high specific capacity (1160 mA-hour g⁻¹), low voltage (−2.714 V), and low cost (US$4 per Kg) of sodium (1–7). Unfortunately, to date, sodium anode still suffers from indisciplined dendrites and infinite volume change during cycle processes, which cause rapid capacity decay, low coulombic efficiencies, and even safety hazards (8–12), imped ing its practical applications in sodium-based batteries.

To alleviate or circumvent the problems of dendrites and infinite volume change of alkali metal anodes, some efficient strategies such as self-heating–induced healing (13) and ideal structural construction (14–21) have been explored. Among them, one is to explore three-dimensional (3D) hosts for metallic sodium, guiding its deposition in a matrix. In this regard, 3D porous graphene frameworks (14, 15), porous carbon materials (16–19), porous aluminum (20), and 3D nickel networks (21) have been used as hosts for metallic sodium, affording various hybrid sodium-based electrodes. Since these 3D hosts can not only decrease the real current density of electrodes but also homogenize the electric field distribution and guide the sodium ion flux, the resultant hybrid sodium electrodes commonly show low voltage hysteresis (25 to 100 mV) and improved cycling stabilities (300 to 1000 hours) (14, 15, 17, 20). For instance, carbonized woods with numerous nanochannels have been developed to control the deposition of sodium, affording a stable sodium anode with a low hysteresis of 30 mV (17). Meanwhile, porous Al foil has also been demonstrated to be favorable for the deposition of sodium, showing a good cycle life (20). Moreover, these 3D hosts enable one to efficiently solve the infinite volume change of sodium, owing to their 3D structures and good chemical stabilities (22–25). However, in most cases, they lack the nucleation seeds of sodium, are unable to control the nucleation of sodium, and further eliminate the sodium dendrites.

Unlike metallic lithium, there are a large number of metal-based seeds such as Au, Ag, and Zn to guide the nucleation of lithium (26–30), sodium has no reported metallic nucleation seeds until now. According to binary phase diagrams between Na and metals (31), we find that only main group II metals such as Be, Mg, and Ba have little solubility in metallic sodium, which may be potential nucleation seeds for sodium, according to Cui’s experiences on metallic lithium anodes (26). Given that these group II metals enable homogeneous dispersion into 3D hosts and have the similar nucleation function to lithium, some 3D hosts may be achieved to solve the issues of both sodium dendrites and infinite volume change.

Here, we experimentally demonstrate that metallic sodium can be controllably deposited onto the main group II metal (Be, Mg, and Ba) foils since they have definite solubility in sodium and enable one to form solid solution surface layers to markedly reduce the nucleation barriers of sodium, guiding the parallel growth of sodium on the foils. This discovery renders us an efficient strategy to eliminate the nucleation barriers of sodium by homogeneously dispersing Mg clusters in a 3D hierarchical structure (3DHS) on the basis of a carbonized Mg-MOF-74 (Mg-based metal-organic framework–74) (cMOF74) membrane. In the case of the 3DHS with Mg clusters, the large number of Mg clusters can act as preplanted nucleation seeds to facely guide the homogeneous nucleation and uniform growth of sodium, and the 3D structure can overcome the volume change issue of Na anode. Thus, a dendrite-free sodium metal anode with a very low potential of 27 mV and a superior cycling stability of up to 1350 hours is achieved on the basis of the 3DHS with Mg clusters.

RESULTS

Nucleation behaviors of sodium metal on main group II metal foils

To investigate the nucleation behaviors of sodium on different metals, we chose typical main group II metal (Be, Mg, and Ba) foils with definite solubility in Na as substrates for the electrochemical deposition of sodium in comparison with common Al and Cu foils without any solubility in Na. As shown in Fig. 1 (A and B), main group II metal foils exhibit much lower overpotentials (36.3, 35.5, and
12.1 mV for Be, Mg, and Ba, respectively) than those of Al and Cu (53.0 and 44.9 mV, respectively) foils, suggesting lower nucleation barriers of sodium on main group II metal substrates. These findings can be further confirmed by morphologies of deposited sodium on main group II metal foils at different deposition stages. As demonstrated in Fig. 1 (C to E), in the initial stage, there are numerous homogenously nucleated sodium on main group II metal foils in the shapes of spheres (Fig. 1, C and D) and domes (Fig. 1E). On the
contrary, as Al and Cu foils were used as substrates, we observed nonuniform sodium nuclei under the same deposition conditions (Fig. 1, F and G), demonstrating the heterogeneous nucleation of sodium on the metal foils without any solubility. Even after a long-term deposition, we observed flat and compact sodium coatings on main group II metal foils without dendrites (Fig. 1, H to J). In contrast, plenty of sodium dendrites were grown on Al and Cu foils (Fig. 1, K and L). These large differences of sodium nucleation behaviors between main group II metals and the other two metals can be attributed to their different solubility in sodium. According to

![Fig. 2. Controllable nucleation and growth of sodium in the 3DHS. (A) Schematic of Na deposition in the 3DHS film with Mg clusters, demonstrating the controllable nucleation and growth of sodium. Detailed nucleation curves of sodium deposition on the 3DHS film (B) with and (C) without Mg clusters at 50 μA cm⁻², showing a very low overpotential of 6.6 mV for the 3DHS with Mg clusters. Side view SEM images for the deposited Na of the 3DHS (D) with and (E) without Mg clusters. (F) Galvanostatic cycling stabilities of Na (black) and 3DHS after sodium deposition (orange) electrodes in symmetric cells at 0.5 mA cm⁻². Inset: Voltage profile at the 50th cycle.](image-url)
phase diagrams, these main group II metals have infinite solubility in sodium, including Be [<0.1 atomic % (at %) at 97.5°C], Mg (<0.1 at % at 97.7°C), and Ba (~1.2 at % at 70°C) (Fig. 1M and fig. S1, A and B), which enable the surface metallic atoms to be dissolved into Na before producing pure Na phase, generating solid solution layers. These layers can serve as buffer layers to effectively eliminate nucleation barriers, guiding facile sodium nucleation, similar to that of Li (25). Comparatively, the solid solution layers are absent in the cases of Al and Cu (fig. S1, C and D), resulting in the nonuniform deposition with high nucleation barriers. These results can be further confirmed by the detailed sodium nucleation behaviors on Mg foil. As shown in fig. S2, the nucleation process of sodium in Mg foil could be divided into four stages (I to IV). Sodium is initially nucleated on the substrate (0.01 mA∙hour cm−2), forming some sodium nanospheres (fig. S2B). Owing to the infinite solubility of Mg in sodium (<0.1 at % at 97.7°C), the contacted Mg surface to the sodium nanospheres should be dissolved into Na nuclei, forming a solid soluble layer (fig. S2, B to E). By increasing the deposition levels of sodium, sodium would prefer to grow around the soluble layer, forming the annular growth of sodium (fig. S2, C and D). Thus, the soluble layer enables guidance on the growth of sodium in the parallel direction to the Mg substrate (fig. S2E). To gain further insight into the influence of solubility of sodium in metals on sodium nucleation, we chose a metal Sr foil (Na has a solubility of ~12.4 at % in Sr at 94°C, but Sr has no solubility in Na; fig. S3B) compared with Mg foil to carefully investigate the nucleation behaviors of sodium. As shown in fig. S2 (F to J), in the case of Sr substrate, the initially deposited Na (0.01 mA∙hour cm−2) is fully soluble in the Sr substrate, forming a solid solution that acts as the solvent, and the Na-Sr alloy becomes solute islands in the substrate (fig. S2G). This should be originated from the high solubility of Na in Sr. By increasing the deposition level of sodium to 0.02 mA∙hour cm−2, the islands rapidly become bigger in length (fig. S2H). By further increasing the deposition level of sodium to 0.04 and 0.10 mA∙hour cm−2, the islands become bigger in both length and particularly height (fig. S2, I and J). This suggests that, preferentially, sodium grew vertically to the substrate once sodium was excessively deposited, forming numerous sodium nanoparticles in the islands. In contrast, in the case of bare Na foil,

Fig. 3. Fast infusion of molten sodium into the 3DHS and production of Na-3DHS. (A) Time-lapse images of molten Na infusion into the 3DHS film. (B) Optical pictures of flexible Na-3DHS. (C) Side and (D) top views SEM images of Na-3DHS, indicating the uniform infusion of sodium into the 3DHS film. (E) XRD patterns, (F) nitrogen sorption isotherms, and pore diameter distributions of the 3DHS film before and after Na infusion. a.u., arbitrary units; STP, standard temperature and pressure. Photo credit: Mengqi Zhu, Beihang University.
Fig. 4. Electrochemical properties of the Na-3DHS. Galvanostatic cycling stabilities of Na-3DHS (orange) and Na (black) electrodes in symmetric cells at (A) 0.5 and (B) 1 mA cm⁻² for 1 mA-hour cm⁻². (C) Stripping/plating curves of Na-3DHS and Na electrodes at the selected 10th cycle at 0.5 mA cm⁻². (D) Stripping/plating curve of the Na-3DHS at the 100th cycle at 0.5 mA cm⁻². Impedance spectra of (E) Na-3DHS anode after 2 and 100 cycles and of (F) bare Na anode after 2 and 10 cycles.
sodium nucleates easily on the Na foil and then rapidly grows vertically along the nucleation, forming numerous sodium dendrites (fig. S2, K to O).

**Controllable deposition of sodium in the 3DHS with Mg clusters**

The discovery of the nucleation behaviors of Na on main group II metals opens up a new opportunity to guide the deposition of Na. In principle, if the main group II metals can be further dispersed uniformly in the 3DHS, then it is anticipated to achieve a dendrite-free sodium anode. Owing to the ultrahigh chemical activity of Ba (figs. S4 and S5) and the high toxicity of Be, we chose Mg as a representative of main group II metals to be further dispersed into a conductive 3DHS by carbonizing Mg-MOF-74 (fig. 2A; for details, see table S1 and figs. S6 to S8) (32–38). We achieved a very low overpotential of only 6.6 mV at 50 μA cm⁻² for the 3DHS with Mg clusters (fig. 2B), which is about one-ninth of the 3DHS without Mg clusters (63.2 mV; Fig. 2C), and is much lower than those of main group II metal foils (12.1 to 36.3 mV). This demonstrates that there is a very low nucleation barrier of sodium deposition in the 3DHS with Mg clusters, leading to a uniform nucleation and growth of sodium in the matrix (Fig. 2D and fig. S9A). In contrast, if Mg species in the 3DHS were removed by acid etching, then numerous sodium dendrites are grown on the surface of the 3DHS (Fig. 2E and fig. S9B). After highly predepositing sodium (6 mA·hour cm⁻²) in the 3DHS with Mg clusters, a hybrid sodium anode could be generated and exhibited a good cycling stability including a low overpotential of ~27 mV at 0.5 mA cm⁻² (Fig. 2F).

**Fabrication and characterizations of the Na-3DHS**

The 3DHS with Mg clusters displays a good “sodiophilic” property with sodium, markedly facilitating the fast infusion of molten sodium into the matrix in a very short time (3 s) and thus affording a uniform Na-3DHS hybrid (Fig. 3A, fig. S11, and movie S1) with a Na content of ~55%. Compared with the original 3DHS film that can be broken easily, the Na-3DHS hybrid exhibits good flexibility, as shown in Fig. 3B. The typical scanning electron microscopy (SEM) images reveal a uniform and smooth surface with a thickness of ~300 μm for the Na-3DHS (Fig. 3, C and D), similar to the initial thickness (fig. S8C), demonstrating that the 3DHS has good chemical and thermal stabilities during the sodium infusion process. To evaluate the composition of this Na-3DHS film, we performed x-ray diffraction (XRD) test. In the case of the Na-3DHS film, there are several identified peaks at 29.6°, 48.2°, and 52.2°, well indexed to (110), (200), and (211) facets of Na, as displayed in Fig. 3E. Meanwhile, there are three visible peaks at 32.2°, 34.4°, and 36.6°, attributed to the (100), (002), and (101) facets of Mg. Moreover, the XRD peaks belonging to MgO are also observed, which should be originated from the oxidization of Mg clusters, owing to their high chemical activity. The product MgO should react with molten Na during our infusion process, rendering the good affinity of the 3DHS with sodium. This can be further confirmed by the 3DHS film without Mg species, on which the molten Na prefers to form a big sphere rather than to infuse into the film (fig. S12). From the highly magnified top and side views of the Na-3DHS film (fig. S13), it is clear that the pores in the 3DHS film were uniformly filled by sodium. This is in good agreement with the Brunauer-Emmett-Teller (BET) analysis, as shown in Fig. 3F. After Na infusion, the Na-3DHS exhibits a much lower surface area (3.9 m² g⁻¹) than that of the 3DHS (347.7 m² g⁻¹).

**Electrochemical performances of the Na-3DHS**

To evaluate the electrochemical properties of the Na-3DHS, we performed galvanostatic cycling of symmetric cells (Fig. 4). We achieved a low overpotential of ~27 mV for the Na-3DHS at 0.5 mA cm⁻² (Fig. 4A). This value is similar to that of the highly deposited Na in the 3DHS and is much lower than that of bare Na (112 mV) and those reported sodium anodes (30 to 100 mV) (12, 13, 16). This Na-3DHS exhibits a good long-term stability of up to 1350 hours, which is about 26 times longer than that of bare Na (51 hours) and is also much longer than those reported sodium-based anodes (300 to 1000 hours) (13, 20). By increasing current density to 1.0 mA cm⁻², the Na-3DHS still maintains a long cycle life of up to ~380 hours with stable plateaus, whereas bare sodium displays a sudden drop of voltage in the initial cycles, owing to the short circuit (Fig. 4B). When the selected voltage curves of the Na-3DHS were magnified (Fig. 4, C and D), flat and stable plateaus are observed, demonstrating the uniform nucleation and deposition of sodium inside the Na-3DHS. Moreover, the Na-3DHS exhibits a stable interfacial resistance after 100 cycles (Fig. 4E), while that of bare Na markedly increases even after 10 cycles (Fig. 4F).

To identify the origin of the superior electrochemical properties of the Na-3DHS, we conducted deep stripping and plating tests. After a deep stripping with a high specific capacity of 10 mA·hour cm⁻², which is ~50% of the whole capacity, a relatively compact film with the original thickness of ~300 μm is visible from the side view, as shown in fig. S16B. From the superficial top view, it is known that some big pores are built from cMOF74 particles (fig. S16D). Through a high plating process, sodium can be reversibly filled back into the pores of the 3DHS film, reforming the uniform Na-3DHS hybrid (fig. S16, E to G). Even after striping and plating for 100 times, the structure and thickness of the Na-3DHS hybrid are still well maintained (fig. S17). Thus, associated with the well-known functions of 3D conductive structure (homogenizing the electric field and Na ion flux distributions) (39–41), it is clear that the uniform stripping and plating process of the Na-3DHS can be ascribed to the presence of abundant Mg clusters in the 3DHS and the unique structure, guiding the facile nucleation and uniform growth of sodium. Moreover, the Na-3DHS can be directly used to construct a cell with a common cathode [Na3V2(PO4)3], exhibiting an ultrastable cycling stability of up to 900 cycles at 10 C rate, while the cell with bare Na anode exhibits a rapid capacity decay (fig. S19). If the cathodes with higher specific capacities such as FeS2 or sulfur were chosen, then the reversible capacity of full cells can be further improved (543 mA·hour g⁻¹ for the FeS2 cathode; fig. S20).

**DISCUSSION**

In conclusion, we demonstrated that there were very low nucleation barriers of sodium with main group II metals such as Be, Mg, and Ba. These are attributed to the definite solubility of main group II metals in sodium, forming solid solution layers that serve as buffer layers for the deposition of sodium. This principle rendered us an efficient strategy to eliminate the nucleation barrier of sodium by homogeneously dispersing Mg clusters in a 3DHS. Thus, a dendrite-free sodium anode with low overpotential and superior cycling stability could be achieved on the basis of the 3DHS with plentiful Mg clusters. Moreover, the infinite volume change could also be efficiently circumvented by the stable 3D porous structure. This thus shed light on the homogeneous
MATERIALS AND METHODS
Fabrication of the Na-3DHS
Initially, Mg-MOF-74 was synthesized as follows: 0.712 g of Mg(NO)3 ·6H2O and 0.167 g of 2,5-dihydroxyterephthalic acid were added into a mixture (N,N-dimethylformamide/ethanol/deionized water, 67.5 ml:4.5 ml:4.5 ml), followed by ultrasonic treatment for 30 min to gain a uniform solution. After heating at 125°C for 26 hours, obtained powders were concentrated by filtration, followed by washing with methyl alcohol three times, and then dried at 60°C for 24 hours. Subsequently, the as-prepared MGMOF-74 powders were heated at 500°C for 3 hours and at 700°C for another 2 hours in H2/Ar, generating cMOF74. The 3DHS film was prepared by pressing the cMOF74 powders. Then, the resultant 3DHS film was contacted with molten Na on one side in an argon-filled glove box, affording a uniform Na-3DHS film. To fabricate the Na-3DHS hybrid with different Na contents, Na foils with different weights were put on the surface of the heated 3DHS film to form hybrid anodes (Na:3DHS, 7:3 and 8:2 weight %). To remove the Mg species in cMOF74, as-prepared cMOF74 powders were washed with hydrochloric acid several times, and the precipitates were collected through filtration and then dried at 60°C for one night.

Characterizations
SEM images were measured with a JSM-7500 SEM and an attached energy-dispersive x-ray (EDX) spectrometer. Nitrogen adsorption/desorption tests were executed with an automated surface area and a pore size analyzer (BET, QUADRASORB evo). The phase composition was carried out at room temperature using XRD with Cu Ka radiation. X-ray photoelectron spectroscopy (XPS ESCALAB 250Xi, USA) tests were conducted to analyze chemical states of samples.

Electrochemical measurements
To investigate the electrodeposition behavior, CR2032 coin cells were assembled with different substrates (Be, Mg, Ba, Cu, and Al foils, as well as the 3DHS with and without Mg clusters) as working electrodes and with bare Na as counter electrodes. The glass fiber membrane was used as a separator, and a common electrolyte [1 M NaClO4 in ethylene carbonate/diethyl carbonate (1:1, volume %), 5% fluororoethylene carbonate] was used; the current density performed was 50 µA cm−2. Galvanostatic cycling tests were conducted in a LANHE electrochemical testing system. To investigate the cycling stability of the 3DHS with Mg clusters after Na deposition, electrodes were prepared by preplating Na (6 mA·hour cm−2) inside the 3DHS with Mg clusters at a current density of 0.25 mA cm−2. To measure performances of full cells, cathodes [Na3V2(PO4)3 and FeS2] were fabricated by mixing active materials, conductive carbon, and binder (mass ratio, 8:1:1) and dried at 60°C overnight. The final areal loadings of the Na3V2(PO4)3 and FeS2 cathodes were 1.61 and 1.23 mg cm−2, respectively.
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