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Perspective—Reversible Magnesium Storage in Silicon: An Ongoing Challenge

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The increasing popularity of rechargeable commercial lithium-ion batteries raises a serious sustainability concern: Relying solely on lithium-ion batteries for the global portable/non-stationary electrochemical energy storage demands will put considerable strain on the resources used in these batteries. Therefore, alternative rechargeable battery technologies, including magnesium-ion batteries, are desirable. Silicon is very attractive for largescale application as a magnesium-ion battery anode due to its high natural abundance and its ultrahigh gravimetric capacity of 3,816 mAh g⁻¹ for magnesium storage in the form of magnesium silicide (Mg₂Si). Despite these unique advantages, to date the reversible electrochemical storage of magnesium in silicon has not yet been demonstrated experimentally, although theoretical studies predict that alloying reactions of silicon with magnesium are thermodynamically possible. The present article is aimed at elucidating the challenge and current status associated with the reversible storage of magnesium in silicon and presenting the future needs to overcome this challenge.

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The rechargeable lithium-ion battery (LIB) technology has revolutionized the way we live, as recognized by the 2019 Nobel Prize in Chemistry.¹ This revolution is now rapidly transforming the transportation industry as depicted by the myriad of battery electric vehicles on the market (e.g. Tesla, Nissan Leaf, Renault Zoe, BMW i3, Chevrolet Bolt EV, Ford Focus Electric, etc...). The widespread popularity of LIB-powered electric vehicles will directly contribute to mitigate our environmental issues, since gasoline-powered vehicles emit nearly one quarter of the U.S. greenhouse gases, making them one of the primary contributors to the global climate change.² On the other hand, relying only on LIBs to power electric vehicles will put considerable strain on lithium, cobalt and nickel resources used in these batteries.^{3–7} In fact, resources used in LIBs are becoming more expensive due to high demand, and the global cobalt market heavily depends on supplies from countries with high geopolitical risks.^{6–11} Therefore, alternative battery technologies other than LIBs are desirable to satisfy our growing demand for energy. Magnesium-ion batteries (MIBs) offer many distinct advantages over LIBs, including the abundance of magnesium, the reversible dendrite-free deposition of magnesium,^{4,12–15} the divalent nature of the magnesium ion, the relatively smaller ionic radius of magnesium ions compared to lithium ions, and finally the fact that magnesium metal is less reactive and thus safer than lithium metal.^{14,16–20} Despite these advantages, magnesium metal is not used as the anode in practical MIBs due to its incompatibility with conventional battery electrolytes.^{13,21–24} As a consequence, instead of magnesium metal, alloys of magnesium are used as the anode in MIBs,^{3,25–27} among which Mg₃Bi₂ (capacity: 385 mAh g⁻¹),²⁶ Mg₂Sn (capacity 903 mAh g⁻¹),^{2,28} Mg₂Ga₅ (capacity: 308 mAh g⁻¹)¹¹ are the most promising candidates. With the exception of Mg₂Sn, commonly investigated alloy-type MIB anodes exhibit a relatively low gravimetric capacity; for new applications such as the above-mentioned battery electric vehicles, high capacity anodes are desirable to reduce the overall mass of the battery without lowering its specific energy density.

Silicon-magnesium and silicon-lithium alloys including Mg₂Si and Li₂₂Si₅ are very attractive as magnesium-ion and lithium-ion battery anodes, due to the high natural abundance of silicon (Si is the 2nd most abundant element in the Earth's crust) and its ultrahigh theoretical gravimetric capacity for magnesium storage (3,816 mAh g⁻¹ for the Mg₂Si phase) and for lithium storage (4,200 mAh g⁻¹ for Li₂₂Si₅ phase).^{29–35} For the sake of comparison, the theoretical capacity of graphite used in commercial LIBs is only 372 mAh g⁻¹, which is roughly one order of magnitude lower than that of silicon. Magnesium and lithium storage in silicon is a diffusion-controlled process, which is extremely sluggish in bulk materials. Therefore, nanoscale silicon instead of bulk silicon is needed to shorten the effective diffusion distance of magnesium and lithium in these host materials.^{29–35} Although various types of nanostructured silicon (nano-Si) including silicon nanoparticles,^{36–38} silicon nanowires,^{33,39,40} and nanoporous silicon,^{29,34,41} have been processed and successfully used as the anodes in LIBs,^{29–34} to date, the reversible electrochemical storage of magnesium in nano-Si has not yet been demonstrated experimentally, although theoretical studies predict that alloying reactions of silicon with magnesium are thermodynamically favorable.³⁵ In the *Current Status* section of this article, we elucidate the main challenge and current progress associated with the reversible storage of magnesium in silicon; and in the *Future Needs and Prospects* section, we suggest a possible approach to overcome this challenge.

Current Status

The reversible storage of magnesium in alloy-type anodes including Mg₃Bi₂,²⁶ Mg₂Sn,^{2,28,42} Mg₂Ga₅,¹¹ and Mg₂Si is governed by mass transport, which involves the solid-state diffusion of Mg ions in or out of the host material (Bi, Sn, Ga and Si). The diffusion of Mg ions in the bulk of the material is extremely sluggish because of its divalent nature, which results in much stronger electrostatic interactions with the lattice of the host material compared with similar electrostatic interactions in the case of monovalent lithium ions. Nanostructured materials^{2,26,28,42} and solid-liquid phase changing materials¹¹ have been proposed to mitigate this issue. In practice, the diffusivity of magnesium in nanostructured host materials is significantly affected by two factors: The native oxide

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or interfacial passive film surrounding the nanostructured material and the characteristic size of this nanostructured material:

- (1) In the former case, the presence of a native oxide or any other type of surface passive film at the interface of nanostructured materials is usually unavoidable, since these surface films automatically form whenever a reactive nanostructured material is exposed to air and moisture during its processing and handling.^{43–47} In the case of silicon for instance, exposed nano-Si will readily react to form a passive native silicon oxide (SiO_2) film,^{43–47} which may result in a core-shell structure, as illustrated in Fig. 1a where the nano-Si (yellow) is surrounded by a passive SiO_2 shell (grey). Such a SiO_2 shell is usually not problematic in lithium-ion battery anodes because monovalent lithium ions can react with SiO_2 during the first cycle and “destroy” it through a *conversion reaction*, during which this SiO_2 is transformed into pure Si and Li_2O .⁴⁸ In the case of MIBs however, the diffusivity of divalent magnesium ions through such passive films is highly unfavorable, due to the strong electrostatic interaction between the divalent magnesium ions and electronic charges in the lattice of the passive film.^{17,49} Thus, in contrast to LIB anodes in which the passive surface film is converted into the corresponding metal or metalloid and Li_2O , passivating surface films are fatal in MIB anodes.
- (2) In the latter case, since magnesium storage in the bulk of nanostructured materials involves solid-state diffusion, the characteristic size of these nanostructured materials is critical. For the sake of illustration, while it can take up to ~ 3 weeks to store magnesium in commercial Sn nanoparticles with average particle size in the range of 150 nm,² this time is significantly reduced to a few hours, if the characteristic size of nanostructured Sn is in the sub-50 nm range.^{28,50,51} In fact, it has been reported that the critical size of nanostructured Sn should be below ~ 50 nm, for magnesium storage to occur at practical rates.^{28,50} Obviously, such a critical upper size limit also exists in nano-Si, but the value has not yet been investigated, to our knowledge.

The issues described in (1) and (2) pertaining to the blocking surface oxide and the critical structure size represent the fundamental challenges that impede the reversible storage of magnesium in silicon. Note that the huge volume changes that occur during charge storage in alloy-type anodes are not discussed in this article, since these volume changes are not critical for the problem addressed in this article, namely the difficulty to reversibly store

magnesium in silicon. Instead, these volume changes are critical for the cycling stability of battery electrodes. The current state-of-the-art solution to overcome these two issues involves the use of nearly “oxide-free” nano-Si as the anode in MIBs. The same solution has been successfully demonstrated in Sn, where various in situ synthesis strategies have been used to produce nearly oxide-free nanostructured Sn directly inside the battery cell. For example, Parent et al.,⁵¹ as well as Chen et al.,⁵⁰ used the SnSb alloy as the anode in MIB and took advantage of the phase separation of SnSb into Sn-rich and Sb-rich phases during cycling to produce nanostructured Sn embedded in the Sb matrix.^{50,51} This in situ generated nanostructured Sn was obviously nearly oxide-free, since during cycling the electrode materials were not exposed to any external environment other than the anhydrous battery organic electrolyte. These authors further observed that the critical size of nanostructured Sn for which magnesium storage is kinetically acceptable was in the range of $\sim 33 \pm 20$ nm.^{50,51} One issue when nanostructured Sn is produced in situ from the phase separation in the SnSb alloy is that the Sb-rich phase cannot store magnesium. This Sb phase is considered “dead” mass in the battery, which is undesirable. To avoid this dead mass issue, Detsi and co-workers proposed the air-free in situ processing of nanostructured Sn directly from bulk Mg_2Sn .^{28,42} In their process, micrometer-sized bulk Mg_2Sn was used as the active material in a MIB half-cell; during the cycling magnesium was removed from Mg_2Sn (and plated onto the counter electrode), resulting in the formation of nanostructured Sn.^{28,42} Here also, the nanostructured Sn produced under these conditions was nearly oxide-free, since the materials were sealed in the battery cell under argon atmosphere with 0.1 ppm of O_2 and 0.1 ppm of H_2O .²⁸ The characteristic structure size for which magnesium storage took place at acceptable rates was also found to be in the range of sub-50 nm.²⁸ These examples illustrate how the issues raised in (1) and (2) were overcome in the case of Sn. A straightforward question is the applicability of the air-free in situ processing strategy to nanostructured silicon. In other words, is it possible to produce nearly oxide-free nano-Si from micrometer-sized bulk Mg_2Si directly inside the battery cell as illustrated Fig. 1b where the starting Mg_2Si (blue) is decomposed into oxide-free nano-Si (yellow) during the first demagnesiation step, and subsequently use this oxide-free nano-Si for reversible magnesium storage?

In order to answer the above question, we made nanostructured Si through air-free selective electrochemical removal of Mg from bulk Mg_2Si parent material with characteristic particle size in the range between 1–10 μm , using a magnesium-ion battery half-cell configuration with the Mg_2Si parent material as the working

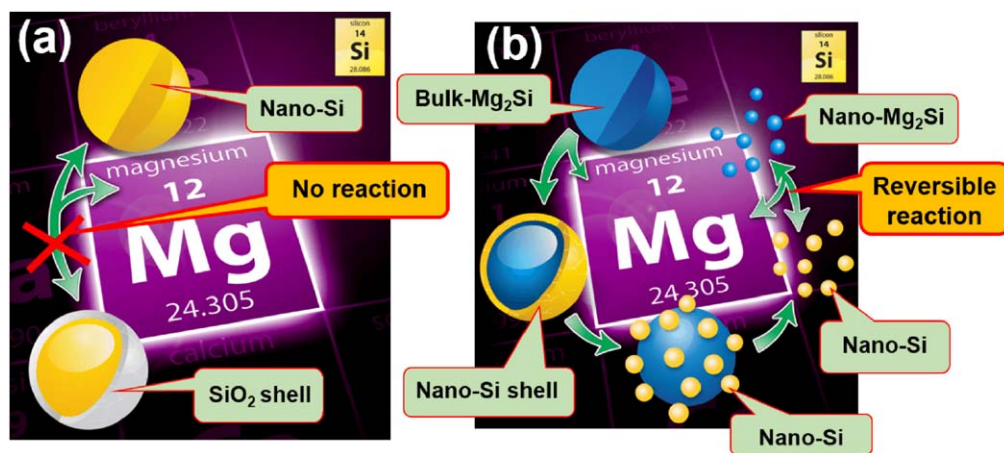


Figure 1. Graphical overview of the issues involving magnesium storage in silicon. (a) The yellow particle represents a nano-Si particle covered with its native oxide SiO_2 (the grey SiO_2 shell around the yellow nano-Si core) used as magnesium-ion battery anode. The SiO_2 shell restricts Mg storage in nano-Si. (b) Instead of using nano-Si coated with its native oxide as magnesium-ion battery anode, one can use micrometer-sized bulk parent materials illustrated by the blue Mg_2Si particle. A bulk Mg_2Si particle will be converted into nano-Si inside the battery cell when the cell is operating (i.e. in situ processing), as depicted by the yellow nano-Si shell around the blue and yellow Si nanoparticle. In this manner, the freshly made nano-Si is nearly oxide-free since the cell operates under inert environment.

electrode (the working electrode is made using a standard battery electrode slurry protocol²⁸), Mg metal as the counter and reference electrodes, and all-phenyl complex (APC) as the electrolyte. The first demagnesian curve of Mg₂Si is shown in Fig. 2a. This demagnesian occurs at a relatively high potential (>1.2 V vs Mg/Mg²⁺) compared with the potential associated with the first demagnesian curve of Mg₂Sn (>0.35 V vs Mg/Mg²⁺) from our previous work.²⁸ Thermodynamically, (de)magnesian of Mg₂Si and Mg₂Sn should occur around 0.1–0.2 V vs Mg/Mg²⁺.^{35,52} This means that the high demagnesian potential of ~ 1.2 V vs Mg/Mg²⁺ recorded in Mg₂Si obviously suggests that Mg removal from Mg₂Si is much more difficult than Mg removal from Mg₂Sn, and requires a very high overpotential. Note that in the case of Sn, the relatively high overpotential is only present during the first demagnesian step, since most of the nanostructured materials are produced during the first cycle.²⁸ Similarly, in the case of Si, we do not expect high overpotentials to occur during the subsequent cycles that will follow the first demagnesian step. It is worth mentioning that when demagnesian results in the formation of a liquid phase anode from a solid phase (i.e. solid-liquid phase transition), the high overpotential is not present during the first demagnesian step, as demonstrated in our recent work in the case Mg₂Ga₅.¹¹

The capacity achieved in Mg₂Si during the first demagnesian step is approximately 3,500 mAh g⁻¹ (see Fig. 2a), which represents $\sim 91.7\%$ of the theoretical gravimetric capacity of Mg₂Si, namely 3,816 mAh g⁻¹. This capacity value suggests that roughly 91.7% of the starting Mg₂Si has been converted into nano-Si, which is much higher than the conversion yield of $\sim 70\%$ achieved in Mg₂Sn (i.e. $\sim 70\%$ of the starting Mg₂Sn was converted into nanostructured Sn in our previous works²⁸).

The typical diffraction patterns of the Mg₂Si composite slurry electrode cast onto a copper foil substrate/current collector are shown in Fig. 2b before (black) and after (red) magnesium removal. The black pattern of the pristine Mg₂Si composite slurry electrode

matches well with the characteristic peaks of carbon (ICDD PDF No. 41-1487) marked by green vertical bars, Mg₂Si (ICDD PDF No. 35-0773) marked by blue vertical bars as well as copper (ICDD PDF No. 04-0836) marked by pink vertical bars. Note that the carbon peak located at $\sim 26.4^\circ$ comes from the carbon materials used as conductive additives in the slurry. The peaks of Cu come from the copper foil used as the current collector/substrate. By comparison, the red pattern of the electrode after the first demagnesian illustrates the disappearance of Mg₂Si peaks with no emergence of new characteristic peaks, which suggests that the pristine Mg₂Si composite slurry has been considerably demagnesian and converted into nanostructured Si during this process. It is worth noting that the absence of Si peaks in the red pattern of the demagnesian nano-Si suggests that the corresponding nano-Si is amorphous, which is not unusual in Si-based battery anodes. Indeed, the transformation of crystalline Si into amorphous Si during electrochemical cycling also occurs in Li-ion battery anodes.^{35,53–57}

The typical scanning electron micrographs of the Mg₂Si particles before and after magnesium removal are shown in Figs. 2c and 2d, respectively, combined with the corresponding chemical composition in the insets, obtained from Energy-dispersive X-ray spectroscopy (EDS). The signal intensity difference depicted from the insets indicates a significant amount of Mg removal from Mg₂Si after the first demagnesian. Besides, it can be seen that after demagnesian, nanostructured Si with characteristic size of ~ 100 nm is formed (Fig. 2d). Al and Cl signals observed on the EDS spectrum after demagnesian (inset Fig. 2d) come from the residual APC electrolyte, trapped in the pores of the fabricated nanostructured Si. Surface characterization techniques including XPS analysis will be performed in the future to further investigate the surface state of the demagnesian material.

The chemical composition of the Mg₂Si composite electrode was further investigated using EDS elemental mapping. Representative EDS maps before and after demagnesian are shown in Figs. 3a

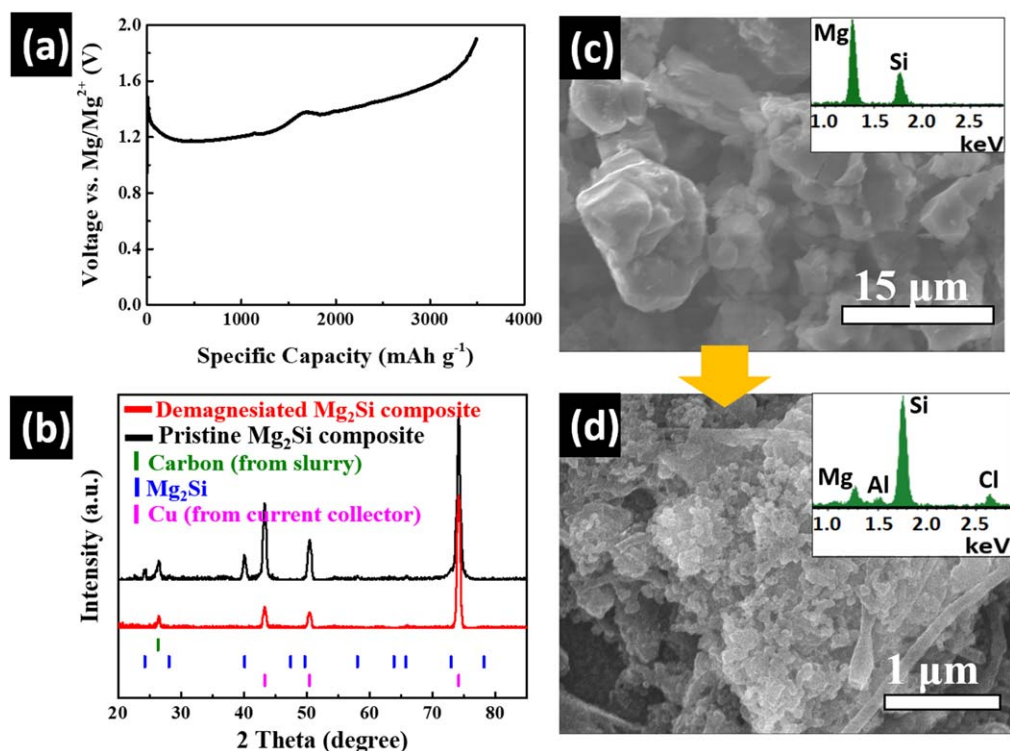


Figure 2. (a) First demagnesian curve of Mg₂Si electrode at the C-rate of C/50. The corresponding gravimetric capacity is $\sim 3,500$ mAh g⁻¹, indicating that $\sim 91.7\%$ of the pristine Mg₂Si has been converted into nano-Si after the first demagnesian step. (b) XRD patterns of the Mg₂Si electrode before (marked in black) and after (marked in red) the first demagnesian step. The difference between the patterns before and after the first demagnesian demonstrates the phase transformation from Mg₂Si to nano-Si, which became amorphous after demagnesian. Scanning electron microscope images and EDS spectra of the Mg₂Si electrode before (c) and after (d) the first demagnesian step. It can be seen that nearly all Mg has been removed from the pristine Mg₂Si, and that nanostructured Si with average feature size in the range of ~ 100 nm has been created after demagnesian.

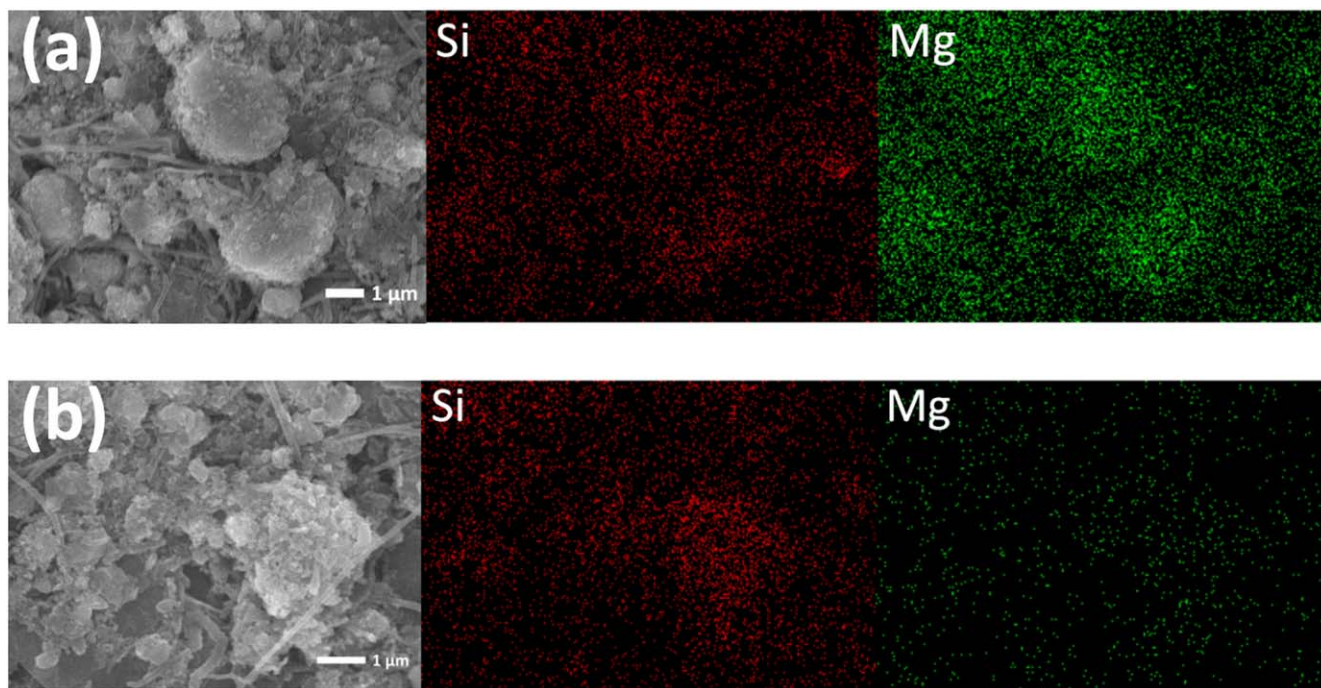


Figure 3. EDS elemental mapping of (a) pristine Mg_2Si particles and (b) demagnesian Mg_2Si particles. For pristine Mg_2Si , the distribution of Si (red) and Mg (green) elements are uniform across the particles, while in the demagnesian Mg_2Si , the particles almost fully consist of Si with minor remaining Mg element.

and 3b, respectively. In the pristine Mg_2Si sample with micron-range particles (Fig. 3a), the distribution of elemental Mg (characterized in green) and Si (characterized in red) across the particles were uniform and chemically indistinguishable. After demagnesian (Fig. 3b), however, the particles almost fully consist of only Si, with only minor Mg signal detected. This agrees with the above-mentioned result that roughly 91.7% of Mg has been removed during demagnesian while 8.3% of Mg were still in the particles.

Future Needs and Prospects

Unfortunately, despite the successful electrochemical demagnesian of bulk Mg_2Si into nearly oxide-free nanostructured Si with feature size in the range of ~ 100 nm, attempts to subsequently reverse the process by electrochemically magnesiating these nanostructured Si were unsuccessful. Thus, based on the current status, it is possible to electrochemically remove magnesium from Mg_2Si , but not to electrochemically introduce magnesium into oxide-free nanostructured silicon with feature size of ~ 100 nm. Knowing that the critical size for reversible Mg storage in oxide-free nanostructured Si was reported to be in the range of ~ 30 – 50 nm,^{28,50,51} we believe that the failure to store magnesium back in the oxide-free nano-Si is explained by the relative large structure size ~ 100 nm of this nano-Si. Therefore, the future needs in the field are: (i) Identifying the critical structure size of Si for which Mg storage can reversibly take place at acceptable rates. This will require both computational simulations and experimental works for validation. (ii) Finding ways to process oxide-free nanostructured Si with size below this critical value, and to demonstrate the reversible storage of Mg in Si.

Summary

Various efforts to develop MIB anodes have demonstrated the successful storage of Mg in materials such as Bi, Sn, Ga, during which Mg_3Bi_2 , Mg_2Sn , and Mg_2Ga_5 are reversibly formed, respectively. However, to date Mg storage in Si—an ultrahigh-capacity anode material—to reversibly form Mg_2Si , has not yet been experimentally demonstrated. In this perspective article, the ongoing

challenges and progress associated with the reversible storage of Mg in Si are elucidated. To further illustrate the issues, we present our work in which micrometer-sized bulk Mg_2Si is successfully demagnesian into nearly oxide-free nanostructured Si with characteristic size around 100 nm; however, Mg could not be introduced back into these nanostructured Si to form Mg_2Si . It is believed that the difficulty to introduce Mg in our oxide-free nanostructured Si is due to its characteristic size being larger than the critical size required for effective magnesiation. From these results, we highlight two important steps in developing a Si MIB anode: (1) The identification of the critical nanostructure size for magnesiation of Si and (2) the development of effective processing routes to synthesize nearly oxide-free nanostructured Si with characteristic size smaller than this critical value. A successful demonstration of an ultrahigh-capacity Si MIB anode will represent a significant step toward the development of high energy density MIBs as an alternative to LIBs.

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