Feasibility of Reversible Electrochemical Na-Storage and Cyclic Stability of Amorphous Silicon and Silicon-Graphene Film Electrodes

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Due to limited lithium reserves in the world as compared to the more widespread and abundant reserves of sodium, there has been recent surge of interests toward the development of Na-ion batteries (SIBs), possibly in lieu of the Li-ion technology.1,2 However, one of the major issues associated with the Na-ion system is that graphitic carbon, the commonly used anode material for Li-ion batteries (LIBs), possesses reversible Na-capacity of just ∼35 mAh g⁻¹.1,3–9 This is an order of magnitude lower compared to the corresponding Li-capacity,3,3–12 and is caused by the larger size of the Na-ion. Accordingly, metallic anode materials, such as Ge, Sb and Sn, have been investigated for SIBs, but without much success in terms of cyclic stabilities due to dimensional changes (and detrimental stress developments) upon Na-alloying/dealloying.3–6

It is a bit surprising that silicon, which possesses possibly the highest theoretical capacity for Li and extensively investigated for LIBs, was hitherto believed to be ‘inactive’ toward sodiation via electrochemical routes.5,7–10,11 Kulish et al.,5 via first principles, showed that sodiation of bulk Si is unfavorable, with Na binding energies being 0.6 eV, along with larger diffusion barrier of 1.06 eV. By contrast, the available Na-Si phase diagram12 indicates that Na-alloying in Si is possible (up to NaₓSi phase); with more recent calculations predicting that one Si atom can host at most 0.76 Na (i.e., up to Na₀.76Si; corresponding to specific capacity of ∼725 mAh g⁻¹).13,14 Such predicted Na-capacity, even though significantly lesser compared to the Li-capacity, would still be considerably superior to those of most other potential anode materials.3,6,15,16 Furthermore, lower Na-intake in Si would result in lower volume expansion compared to the case of Li-intake (viz., ∼114% for Na vs. ∼400% for Li),11 which might just lead to lesser problems related to stress induced degradation and capacity fade in the case of Na.

Due to the earlier belief concerning electrochemical Na-insertion being difficult in Si,1,12–14,18 only very recently few experimental works12,17,18 have explored the possibilities of electrochemical sodiation/de-sodiation in crystalline (c-Si)5,17 and amorphous Si (a-Si)12–14 in the form of nanoparticles. Indeed, both Ellis et al.7 and Komaba et al.,8 in their studies with Si particle sizes of 325 mesh and ∼100 nm, respectively, found that electrochemical sodiation of c-Si particles is difficult. By contrast, less than an year back, Xu et al.19 reported that reversible uptake of Na in c-Si nanoparticles is possible (with reversible capacity of ∼250 mAh g⁻¹), albeit at much reduced particle sizes of ∼20 nm; which would throw significant processing/handling challenges (in addition to lower tap densities).

In another very recent work by Lim et al.,12 coating of a-Si by Sn led to net Na-capacities of ∼230 mAh g⁻¹, even though bare Si hardly showed any Na-capacity. With respect to Si-based composite electrodes, Zhao et al.16 reported Na-capacity of ∼280 mAh g⁻¹ (after 100 cycles) for mechanically milled a-Si/C electrodes, but which would correspond to ∼100 mAh g⁻¹ for a-Si alone after removing the contribution from carbon.

Accordingly, the Na-capacity of a-Si as stand-alone active material, which may be achievable under experimental conditions, is yet to be confirmed. Furthermore, the experimental results seem to indicate, but without throwing much insight into, possible ‘size effect’ for sodiation (and Na-capacity). Against these backdrops, in the present work we have used continuous films of a-Si, without any binder/additive, of three different thicknesses (viz., 250, 100 and 50 nm) as electrodes and performed systematic studies in ‘Na half cells’, coupled with analytical computational studies, to develop insights into the reversible Na-capacity, Na-diffusivity and electrochemical cycling performance achievable with a-Si alone. Additionally, the effects of presence of well-ordered few layers graphene as interlayer between a-Si and current collector on the Na-capacity and cyclic stability have also been investigated for the first time.

Experimental

Thin film depositions.—Silicon films were deposited via E-beam evaporation (Hind Hi-Vacuum Systems) on copper foils (0.025 mm thick; 4 cm² area; Sigma Aldrich), which were cleaned before deposition with deionized water, acetone and propanol, followed by rinsing with dilute HF (to remove any surface oxides). The Si films of desired thicknesses (viz., 250, 100 and 50 nm) were grown using deposition rate of 0.7 Å s⁻¹ for different durations (viz., 60, 25 and 12.5 min, respectively), with the thicknesses being precisely monitored using a built-in thickness monitoring system. The mass of the electrodes were

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confirmed not only by measuring the same before and after deposition using a precision mass balance, but also by cross-checking based on the measured film thicknesses and known density of a-Si (i.e., $\sim 2.3 \text{ gm cm}^{-3}$). Few layers graphene (FLG) films were grown on the same Cu foils via chemical vapor deposition route at 1000°C using methane gas as precursor, in the continuous flow of H$_2$+N$_2$ (1:9) as carrier gas. Under the optimal growing conditions and with 30 min as deposition time, $\sim 7$ well-ordered continuous graphene layers were obtained, as detailed in our previously published work.$^{19}$

Characterization of the Si films.—The as-deposited Si films were characterized using grazing incidence X-ray diffraction (GIXRD; using Cu K$\alpha$) (Rigaku Smartlab) and Raman spectroscopy (wavelength 532 nm; WITec alpha300). The surface features were observed using FEG-SEM (JEOL-JSM 7600F). The film thicknesses were confirmed using precision mass measurements and cross-section imaging using dual-beam focused ion beam (FIB-SEM) (Auriga compact, Carl Zeiss).

Cell assembly and electrochemical cycling.—The a-Si and a-Si/FLG films on copper foils were cut into circular discs (14.5 mm diameter) and assembled against sodium metal (counter/reference electrode) in CR2032 coin cells in Ar-filled glove-box (Jacomex; GP-Campus). 1 M NaClO$_4$ in EC:DMC:DEC (1:1:1) (Sigma Aldrich) was used as electrolyte and glass microfiber filter paper (Whatman; Grade GF/D) as separator. Galvanostatic cycling (at current density equivalent to C/10) and cyclic voltammetry (at voltage sweep rate of 0.05 mV/s) were performed within the potential range of 0.01 to 2.0 V vs. Na/Na$^+$ using Autolab204 potentiostat/galvanostat.

Results and Discussion

Basic features of the as-deposited Si films.—GIXRD patterns (Figs. 1a, 1b) did not show any crystalline Si peak. Raman spectra (Figs. 1c, 1d) showed the highest intensity peak at $\sim 478 \text{ cm}^{-1}$ (for a-Si; not at $\sim 521 \text{ cm}^{-1}$ for c-Si), along with the other characteristic peaks for a-Si, viz., the TA, TO, LA and LO at the respective positions;

![Figure 1](image_url)
thus further confirming the amorphous nature of the Si films. In the case of a-Si/FLG films, the characteristic peaks for FLG (viz., D, G and 2D peaks) could also be seen. More details concerning the well-ordered nature of the ~7 graphene layers having interlayer spacing of ~0.34 nm can be obtained from our previously published work.19 The SEM observations showed continuous and crack/pore free surfaces for the as-deposited a-Si films (Figs. 1e, 1f).

**Electrochemical behavior of a-Si films, sans FLG interlayer.**—Cyclic voltammograms (CVs), recorded with the a-Si films, showed irreversible peaks at ~1.5, ~0.8 and ~0.5 V in the first cathodic scans, which got totally suppressed from the 2nd cycle onwards (Fig. 2a). These features are likely to be associated with surface reactions, including SEI layer formation and possible reduction of native oxide layer. More importantly, the CVs tend to suggest that electrochemical Na-alloying in a-Si takes place from below ~0.6 V against Na/Na⁺, whereas de-alloying takes place over a broader potential range from above ~0.7 V to ~1.5 V. Here it is also interesting to note that for the 250 nm thick a-Si film electrode, the sodiation/de-sodiation currents seem to be greater after 100 cycles, as compared to the currents recorded in the initial cycles. The inferences from the CVs were well supported by the galvanostatic discharge/charge profiles (see Figs. 2b–2d), which also show suppression of irreversible phenomena from the 2nd cycle onwards and occurrence of reversible sodiation/de-sodiation below/above ~0.6/0.7 V vs. Na/Na⁺.

With respect to the reversible (or de-sodiation) capacities as functions of discharge/charge cycle numbers (Figs. 3a–3c), the first cycle capacity recorded with the 250 nm thick a-Si film was merely ~40 mAh g⁻¹; which at that point seemed to be in line with the earlier belief of electrochemical sodiation/de-sodiation in Si being rather impossible. Interestingly, the capacity started increasing from the 2nd cycle onwards, reaching a value of ~155 mAh g⁻¹ in the 27th cycle, which remained almost constant till the 42nd cycle (Fig. 3a); subsequently decreasing with further cycling to ~90 mAh g⁻¹ (more than double the 1st cycle capacity) after 100 cycles. Coulombic Efficiency (CE) also seems to have a trend somewhat similar to that of the Na-capacity; increasing from just ~25% in the 1st cycle to ~100% by the 25th cycle; subsequently decreasing marginally to ~95% up to the 100th cycle. Overall, the cycling results with the 250 nm a-Si films are themselves fairly encouraging since they confirm that reversible electrochemical Na-alloying is possible, with some capacity retention even till 100 cycles. It is to be noted here that the reversible Na-capacities recorded in this work are not expected to have contribution from sources other than a-Si due to the simple electrode architecture (continuous films, sans binder/additive).

Nevertheless, the observation concerning increase in Na-capacity for the 250 nm thick film from the 2nd cycle, which appears like continued ‘activation’ of a-Si during sodiation/de-sodiation, need to be better understood. Here we refrain from being too speculative with respect to the possible causes. However, in case the observed ‘activation’ like behavior is partly due to Na-insertion/removal being initially transport limited through the a-Si film (as predicted via computational studies8,9), reducing the film thickness is expected to suppress such occurrence, in addition to improving the overall specific Na-capacity.

In this context, thinner a-Si films (viz., 100 and 50 nm thick) were cycled under similar conditions; and it is encouraging that the observations, as in the following, supported the above hypothesis. For the 100 nm film (see Fig. 3b), the first de-sodiation capacity was ~450 mAh g⁻¹; which is an order of magnitude and three
times greater than the first de-sodiation and the maximum capacities (i.e., in the 27th cycle), respectively, recorded with the 250 nm film. More importantly, contrary to the case of the 250 nm thick film, no increase in Na-capacity or ‘activation’ was observed for this thinner film; with the Na-capacity continuously decreasing with cycling to ∼70 mAh g\(^{-1}\) at the end of 100 cycles (also, CE increased continuously from initial value of ∼35% to >95%). Even though the ‘activation’ like step could be avoided, the Na-capacity retention was rather poor, with only ∼16% of the 1st cycle capacity being retained after 100 cycles (not surprising for such alloying reaction based electrodes).

Similar to the case of the 100 nm thick film, no ‘activation’ like behavior was observed during cycling of the still thinner 50 nm a-Si film (see Fig. 3c). These observations tend to support the hypothesis that the observed ‘activation’ for the 250 nm film was, at least partly, related to the overall Na transport limitation. In this context, it is also believed that upon electrochemical Na-insertion/removal, the active a-Si film gets cracked (thus partly reducing the Na transport distances) and also ‘expanded’ irreversibly (similar to that reported in the case of Li-insertion/removal\(^{20}\)), thus improving the overall Na transport kinetics with progress in cycling. This, in fact, becomes particularly apparent (and dominant in the initial cycles) for the thickest a-Si film used here (i.e., the ∼250 nm thick film), sodiation/desodiation of which is severely Na transport limited at the beginning, and which also shows greater severity of cracking (compare Figs. 3d, with 3e and 3f).

From the performance point of view, starting with a de-sodiation capacity similar to the 100 nm film in the 1st cycle, ∼125 mAh g\(^{-1}\) Na-capacity could be retained after 100 cycles in the case of the 50 nm film; i.e., somewhat improved Na-capacity retention of ∼37%. Even though cracks could be observed during SEM observations of all the a-Si films discharged/charged for 100 cycles (after removal of surface films following procedure described earlier\(^{20,21}\)), severity of ‘damage’ was lesser for the thicker films (see Figs. 3d–3f). Another important observation is that, despite being partly cracked, the films appeared to remain intact and not delaminated even after 100 cycles, unlike observations usually made with such a-Si films upon repeated lithiation/delithiation cycles.\(^{20,21}\) Overall, the present results/observations indicate in very strong terms that, even though reversible electrochemical Na-alloying is possible in a-Si, dimensional scale of the active material (when used as stand-alone) is a very important criterion with respect to the performance; with preferred dimensions being below ∼50 nm.

**Estimation of the Na-diffusivity in a-Si electrodes via analytical computation studies.**—As mentioned earlier, diffusion coefficient (D) of \(7 \times 10^{-14} \text{ m}^2 \text{s}^{-1}\) was reported by Jung et al.,\(^{11}\) via ab-initio studies, for diffusion of Na in Si. This appears a bit too high, even when compared to the reported Li diffusion coefficients in Si (\(\sim 1 \times 10^{-16} \text{ m}^2 \text{s}^{-1}\))\(^{22}\) (especially, considering that the size and mass of Na are greater than that of Li). Additionally, in one of the classical works, McCaldin et al.\(^{23}\) reported Na diffusivity in crystalline Si (c-Si) to be of the order of \(\sim 6 \times 10^{-16} \text{ m}^2 \text{s}^{-1}\), even at considerably higher temperature of 800°C. In a more recent work, Chou et al.\(^{24}\) predicted that the Na diffusion coefficient is likely to be of the order of \(\sim 10^{-26} \text{ m}^2 \text{s}^{-1}\), but again in c-Si. Our observations of electrochemical Na-storage behavior in a-Si continuous film electrodes (as reported in the previous section) suggest that electrochemical Na-storage in a-Si may also be diffusion limited.

In this context, using analytical computation studies, we have attempted here to get an estimate for the possible overall diffusivity (at least the order of magnitude) of Na in such a-Si electrodes by evaluating the time that would be needed for complete de-sodiation of 50 nm thick film (based on the experimentally achieved de-sodiation capacity; see Electrochemical behavior of a-Si films, sans FLG interlayer section) for various diffusion coefficient values. Such estimation is possible due to the simple model architecture (continuous films, sans binder/additive) of the electrodes used. Assuming that negligible residual Na remains within the a-Si film after complete de-sodiation half cycle, the diffusivity value that results in estimated de-sodiation time similar to that experimentally recorded is believed to be indicative of the order of magnitude of the diffusion coefficient of Na in such a-Si electrodes. The computation has been performed considering 50 nm thick film because of the better reliability of the experimental results (based on galvanostatic cycling) in the context of the Na transport distance (considering that cracking, if any, would be minimum for the same). For the same reason, the first cycle experimental de-sodiation capacity (i.e., ∼340 mAh g\(^{-1}\) or ∼0.45 times the theoretical Na-capacity of 725 mAh g\(^{-1}\)) has been used for the calculations and...
the experimentally recorded de-sodiation duration of \( \sim 15400 \) s (at constant current of 1.7 \( \mu \)A) has been used for the comparison.

The sodium concentration profiles in Si film were derived using one dimensional Fick’s law, as per Equation 1:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad 0 \leq x \leq l \; ; \; t \geq 0
\]  

[1]

Where, \( C \) is the concentration of sodium in silicon, \( t \) is time, \( D \) is the diffusion coefficient, \( x \) is the direction in which concentration is varying and \( l \) is the thickness of the film (50 nm in this case).

The initial and boundary conditions for solving the Equation 1 are:

\[
C(x, 0) = 0, \quad D \left. \frac{\partial C}{\partial x} \right|_{x=0} = 0, \quad D \left. \frac{\partial C}{\partial x} \right|_{x=l} = -f
\]  

[2]

where, \( f \) is the sodium flux at the top surface of the Si film. The flux, \( f = \varphi FA \), where \( \varphi \) is the constant current applied (i.e., 1.7 \( \mu \)A), \( F \) is Faraday’s constant and \( A \) is the surface area of the electrode in contact with the electrolyte (i.e., 1.65 cm\(^2\)). The geometry and related parameters used for the computation has been schematically shown in Fig. 4a.

The non-dimensional forms of concentration, time and thickness, in the same sequence, are shown in Equation 3:

\[
\hat{C} = \frac{C}{C_b}, \quad \hat{t} = \frac{D_0 t}{l_0^2}, \quad \hat{x} = \frac{x}{l_0}
\]  

[3]

Where, \( C_b = 725 \) mAh g\(^{-1}\) (i.e., the theoretical Na-capacity in Si), \( l_0 = 50 \times 10^{-9} \) m and \( D_0 = 0.25 \times 10^{-14} \) m\(^2\) s\(^{-1}\). The values of \( D_0 \) and \( l_0 \) are chosen in such a way that the numerical values of \( t \) and \( \hat{t} \) are equal. Substituting the expressions of Eq. 3 into Eqs. 1 and 2 results in the non-dimensional diffusion equation with initial and boundary conditions, as shown in the following Equations 4 and 5, respectively:

\[
\frac{\partial \hat{C}}{\partial \hat{t}} = \frac{D}{D_0} \frac{\partial^2 \hat{C}}{\partial \hat{x}^2} \quad 0 \leq \hat{x} \leq 1 \; ; \; \hat{t} \geq 0
\]  

[4]

\[
\hat{C}(\hat{x}, 0) = 0, \quad D \left. \frac{\partial \hat{C}}{\partial \hat{x}} \right|_{\hat{x}=0} = 0, \quad D \left. \frac{\partial \hat{C}}{\partial \hat{x}} \right|_{\hat{x}=1} = \frac{l_0 f}{C_b}
\]  

[5]

The non-dimensional concentrations as functions of non-dimensional times (\( \hat{t} \) and non-dimensional positions or thicknesses (\( \hat{x} \)) were estimated by solving Eqs. 4, 5 for different diffusion coefficients. Therefore, to estimate the approximate value of diffusion coefficient of Na in a-Si, the overall capacities (in terms of Na concentration) and the times required for complete de-sodiation were evaluated for the non-dimensional concentration to eventually become zero for different diffusion coefficients. Some of the associated concentration profiles and the results have been presented in Figs. 4b and 4c. As can be seen from the figures, the desodiation times for diffusion coefficients (\( D \)) of \( 7 \times 10^{-14} \) m\(^2\) s\(^{-1}\) (as reported in Ref. 11), \( 1 \times 10^{-13} \) m\(^2\) s\(^{-1}\) and \( 2.4 \times 10^{-19} \) m\(^2\) s\(^{-1}\) are 13700 s, 14100 s and 15400 s. Hence, the de-sodiation time corresponding to the Na-diffusivity value of \( 2.4 \times 10^{-19} \) m\(^2\) s\(^{-1}\) agrees nearly perfectly with the experimental result.

Even though no information is available in the open literature concerning Na-diffusivities in SEI layers formed on a-Si electrodes in Na ‘half/full cells’, in a very recently reported work\(^{25}\) Na-diffusivities in some of the components of the SEI layer formed on Sn electrode in Na ‘half cells’ (again, coin cells containing NaClO\(_4\) in EC/DEC as...
electrolyte) have been estimated to be of the order of $10^{-10}$ m$^2$ s$^{-1}$. Those values are significantly greater (by $\sim 9$ orders of magnitude) than the overall diffusivity value (of $\sim 10^{-19}$ m$^2$ s$^{-1}$) estimated with our a-Si film electrodes. Nevertheless, it is still acknowledged that such simple estimation, as reported here, may not yield a very correct value for the diffusivity of Na in a-Si material per se, primarily since it does not take into account whether any surface film (such as SEI; though expected to be very thin in the first cycle) or stress buildup might also partly contribute toward limiting the overall transport. Despite such reservations, it can be stated here that the relatively lower diffusivity value (of the order of $\sim 10^{-19}$ m$^2$ s$^{-1}$), as predicted by these calculations, agrees well with the experimental results that suggest electrochemical sodiation in a-Si electrodes being diffusion limited. If true, the need for developing a-Si active electrode materials in ‘ultra-fine’ nanoscaled dimensions will be very stringent in order to achieve practically useful Na-capacities in a-Si based anodes.

**Electrochemical behavior of a-Si films, with FLG as interlayer.**—Having confirmed the possibility of electrochemical reversible Na-insertion in a-Si, despite the ‘transport limitation’, the next step was to try and improve the cyclic stability. Accordingly, continuous thin film of few layers graphene ($\sim 7$ layers$^{19}$) was ‘incorporated’ in-between the active a-Si film and Cu current collector; a strategy which has been successfully used in the case of Li-alloying in a-Si.$^{20,26}$ The presence of the FLG interlayer did not result in any notable change in the discharge/charge profiles, which is not surprising considering that graphenic carbon film as thin as $\sim 2$ nm is hardly expected to contribute toward the overall electrochemical behavior; especially in the case of Na-insertion.

The Na-capacities recorded during 100 cycles for the a-Si/FLG films (as presented in Figs. 5a–5c) also show an overall ‘size effect’ for the capacity similar to the case of a-Si, sans FLG. However, a notable observation is the absence of initial ‘activation’ like behavior or increase in Na-capacity with cycling in the presence of FLG, even for the 250 nm thick a-Si film. Although the mere presence of a graphene-based interlayer is not expected to aid Na-transport, it may be recalled here that even in the case of Li-insertion presence of similar interlayer was observed to enhance the Li-capacity in a-Si films (of same thickness).$^{20}$ This was attributed partly to preferential segregation of Li at the a-Si/graphene interface toward the beginning of lithiation$^{27,28}$ (but nothing concerning Li-insertion in-between the individual graphene layers), leading to the possibility of simultaneous Li-insertion in a-Si from two surfaces (i.e., the one in contact with electrolyte; and the other in contact with graphene) and accordingly ‘shortening’ of the overall transport distance through the a-Si film. Even though, unlike in the case of Li,$^{27,28}$ whether Na gets preferentially segregated at the a-Si/graphene interface is yet to be known, the above observations do not rule out such possibility. If valid in this case, it is also expected that the overall Na-capacities get enhanced in the presence of FLG interlayer; which indeed agrees with the present observations. Accordingly, the initial reversible Na-capacities recorded with the 250 and 50 nm films are $\sim 250$ and $\sim 600$ mAh g$^{-1}$; which are nearly double the corresponding maximum capacities recorded in the absence of FLG interlayer (compare Figs. 3a–3c and 5a–5c).

With respect to cyclic stability, the presence of FLG considerably improved the same even for the 250 nm thick a-Si film, leading to retention of $\sim 120$ mAh g$^{-1}$ reversible Na-capacity (i.e., capacity retention of $\sim 48\%$) after 100 cycles (along with CE of $\sim 98\%$). Such performances, being among the better reported to-date for potential anode materials for Na-ion batteries, indicate that in the presence of such interlayers going down to ‘ultra-fine’ nano-sizes may not be needed. Nevertheless, possibly the most significant result of the present work is the performance recorded with the 50 nm a-Si/FLG film electrode, which retained reversible Na-capacity of $\sim 240$ mAh g$^{-1}$ at the end of 100 cycles ($\sim 90\%$ higher Na-capacity compared to the 50 nm a-Si film, sans FLG). Post-cycling (i.e., after 100 cycles) SEM observations of the a-Si/FLG films indicate that cracking got considerably suppressed for all the a-Si film thicknesses in the presence of FLG interlayer; with hardly any degradation/cracking being observed for the 50 nm thick a-Si/FLG film (see Figs. 5d–5f).

If looked closely at the coulombic efficiency (CE) data appearing in Figs. 3 and 5, it can be noted that fluctuations in the CE are considerably greater in the absence of the graphene-based interlayer. Additionally, the fluctuations are also greater for the thickest films used here (i.e., 250 nm thick films). Even though it cannot be stated with certainty, such fluctuations in the CE may partly be manifestations of the cracking taking place during electrochemical cycling, which lead to instability in the SEI layer and repeated occurrence of irreversible surface reactions, including SEI layer formation, at the exposed surfaces. Accordingly, as mentioned above (and also in
Electrochemical behavior of a-Si films, sans FLG interlayer section), the propensity for cracking gets considerably suppressed, and so does the fluctuations in the CE, not only in the presence of the graphene-based interlayer, but also for the thinner a-Si films (viz., the 50 and 100 nm thick films, as compared to the 250 nm thick films).

Such suppression of cracking of the a-Si film, and concomitantly the improved cyclic stability, in presence of the FLG interlayer between the a-Si film and Cu current collector suggests that the graphene-based interlayer helps alleviating the negative impact of the stresses that get developed in the a-Si film due to the dimensional changes upon electrochemical Na-insertion/removal, similar to the case of Li-insertion/removal.20,26,28 In our previously published work,20 which was primarily focused on understanding such phenomena by way of monitoring the stress developments in real-time during electrochemical Li-insertion/removal, the relatively weaker interface between a-Si film and graphene (as compared to the interface between a-Si and current collector) leading to suppression of flow of the otherwise cracked a-Si film and the possibility of individual graphene layers (bonded by weak Van der Waals forces) sliding against past each other in response to the expansion/contraction of the a-Si film were deemed responsible for the improved integrity of the a-Si film. Even though we do not intend to be too speculative here and that such stress monitoring is beyond the scope of the present manuscript, in light of the fact that the presence of similar graphene-based interlayer (again in continuous a-Si film electrode) has also resulted in improving the integrity and cyclic stability of a-Si film upon electrochemical sodiation/de-sodiation, similar role played by the graphene-based interlayer may not be ruled out. More importantly, to the best of our knowledge, this is possibly the best performance ever reported with Si-based anode materials for Na-ion batteries. Elec-

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Conclusions

In summary, we have provided important insights into the feasibility of usage, the issues and the ways to improve electrochemical performance of a-Si based anode materials for Na-ion batteries. Electrochemical cycling of continuous a-Si films with varying thicknesses (sans binder/additive; i.e., sans any possible interference w.r.t. Na intake/capacity) have confirmed that reversible Na-alloying do take place in a-Si; but which are likely be 'transport limited', especially for dimensions (in this case, thicknesses) greater than ∼100 nm. Decent performances, such as initial reversible Na-capacities of ∼340 mAh g⁻¹ with retention of ∼120 mAh g⁻¹ after 100 cycles, could be recorded with 50 nm thick a-Si film. Analytical computation studies have indicated that the overall diffusivity of Na in such a-Si-based electrodes may be of the order of ∼10⁻¹⁹ m² s⁻¹.

Interestingly, the 'transport limitation' related issues got suppressed, leading to considerably enhanced Na-capacities even for 250 nm thick film, in the presence of ∼2 nm thick continuous few layers well-ordered graphene film (FLG) as interlayer between a-Si film and current collector. The 50 nm thick a-Si film, in the presence of the FLG interlayer, showed reversible (i.e., desodiation) Na-capacity of ∼600 mAh g⁻¹ in the 1st cycle. Significantly improved cyclic stabilities were also recorded in the presence of FLG interlayer. Accordingly, at the end of 100 cycles, the reversible Na-capacities recorded with the 250 and 50 nm films were ∼120 and ∼240 mAh g⁻¹. Such Na-capacities and cyclic performances (especially for the 50 nm thick a-Si/FLG; with contribution just from a-Si) are not only the best reported to-date for Si-based anode materials (with the capacities being contributed solely by the a-Si), but also compare with the very best reported so far for Na-ion battery anode materials, in general. Accordingly, this study is expected to pave the way toward further development of high performance a-Si based anode materials for Na-ion batteries.

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