Recent progress in first-principles simulations of anode materials and interfaces for lithium ion batteries

Mathew J Boyer and Gyeong S Hwang

CrossMark

Lithium ion batteries are currently a principal power source for small portable electronics. However, in order to extend their effective use as large-scale energy storage systems for electric vehicles and renewable energy, there is an imminent need to further increase the energy density, power density, and cycle life while retaining safety and cost at an affordable range. This fundamentally represents a knowledge and materials challenge that needs to develop a deeper understanding of electrode and electrolyte materials as well as their interfaces. Here, we briefly review recent progress in first-principles computational studies on the lithiation behavior of anode materials and the structural and chemical evolution of anode/electrolyte interfaces.

Address
Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78712, USA

Corresponding author: Hwang, Gyeong S (gshwang@che.utexas.edu)

Introduction

In the past few decades, lithium ion batteries (LIBs) have attracted considerable attention as power sources for portable electronics and electrical vehicles (EVs). They have several advantages over other secondary battery technologies such as nickel-cadmium (NiCd) and nickel metal hydride (NiMH), including high operating voltage, high energy density, light weight, long cycle life, and zero to low memory effect. LIBs are currently one of the most commonly used rechargeable batteries for small portable electronic devices [1]. However, in order to extend their effective use as large-scale energy storage systems for EVs and renewable energy, there is an imminent need to further increase the energy density, power density, and cycle life while retaining safety and cost at an affordable range. This fundamentally represents a knowledge and materials challenge. The challenge needs to develop a firm understanding of the electrode and electrolyte materials

and the structure and chemistry at their interfaces that will allow us to identify and assess alternative energy storage strategies, in addition to improvements of existing technologies [2•].

Recently with advances in computing power and computational methodology, first-principles based computer simulations have been applied to evaluate the properties and performance of potential candidate materials for both electrodes and electrolytes and better understand the structure, chemistry, and dynamics at electrode/electrolyte interfaces. Computer simulations support and complement experimental studies, and vice versa. They can provide explanations for experimental observations and guidelines for synthesizing and characterizing new materials and developing improved materials systems, while experimental data are used for validating calculation results and testing theoretical predictions. The basic understanding gained from theoretical studies combined with experiments will be crucial for realizing next-generation electrical energy storage systems with long life at an affordable cost. In this article, we briefly review recent progress in first-principles based atomistic simulations of lithiation behavior in carbon-based and silicon-based nanomaterials for LIB anodes and structural and chemical evolution at anode/electrolyte interfaces.

Anode materials: lithiation processes and properties

At present, graphite-based materials are commonly used as anode materials in commercial LIBs due to their long cycle life, low cost, and abundance, but exhibit relatively low gravimetric and volumetric specific capacity [3]. The theoretical capacity of graphite is 372 mAh/g for LiC_6 [2•]. Carbon nanostructures including graphene, reduced graphene oxide (rGO) and carbon nanotubes (CNTs), along with graphene-based composites, have been widely explored as alternatives to graphite. Graphene-based materials have been of particular interest because of their high specific surface area, high electrical conductivity, and excellent mechanical flexibility. The specific capacities and charge rates of carbon-based anodes have been studied using various simulation techniques including density functional theory (DFT) [4], reactive force field based molecular dynamics (ReaxFF MD) [5], and grand canonical Monte Carlo [6].

Although the capacity limitations of carbon-based anodes for use in advanced LIBs need to be overcome, silicon (Si) has emerged as one of the most promising anode materials

because of its abundance, nontoxicity, desirable electrochemical potential to be coupled with high-voltage cathode materials, and more importantly the highest known specific Li storage capacity (close to 4000 mAh/g for Li_xSi, $x \leq 4.4$) which is one order of magnitude higher than that of graphite. However, the practical use of Si as an anode material is hampered by its large volume expansion (~400%), causing pulverization, loss of electrical contact, and consequently early capacity fading; for graphite anodes, the only structural change is a ~12% isotropic expansion. Considerable efforts have been made to overcome these problems, for instance, through structural modifications such as amorphous phases [7,8•] and nanostructured Si [9,10•], combining Si with carbonaceous materials (Si–C) [11–13], alloying Si with active/inactive elements [14,15], and Si oxides (SiO_x, $x < 2$) [16–20]. However, many fundamental aspects regarding the lithiation processes and properties remain unclear since direct characterization of the complex electrochemical systems is rather difficult. Over the last few years, the lithiation mechanisms and electrochemical properties of Si-based nanomaterials have been extensively explored using first-principles based atomistic simulations.

DFT calculations were used to evaluate how Li incorporation affects the electronic structure and bonding nature of the host Si lattice [21,22,23•]. Upon Li incorporation, the bonding strengths among neighboring host atoms are weakened, attributed to the transferred charge from Li. Because of the repulsive interaction, Li cations tend to

remain isolated and well dispersed in the Si matrix. With increasing Li content, the tetrahedrally bonded Si network undergoes disintegration into low-connectivity clusters of various shapes, as shown in Figure 1. Due to the softening of Si network, the bulk modulus is found to decrease almost linearly with increasing Li content. According to DFT calculations, the favorable alloy formation occurs around 71 at.% Li for the crystalline phase and 60–80 at.% Li for the amorphous phase. The crystalline Li–Si alloys are predicted to be about 0.1 eV more favorable than their amorphous counterparts. However, lithiated Si beyond the first charge cycle is most likely to remain in the amorphous phase due to the sizable kinetic barrier for recrystallization at room temperature. The differences in the lithiation behavior between Si and other group IV elements (Ge and Sn) have been also addressed using DFT-based computational approaches [24,25].

Si nanostructures can accommodate larger strain and provide better mechanical integrity because their dimensions would limit the size and propagation of cracks, which typically initiate the fracture process. It has been reported that Si nanowires (NWs) and thin films exhibit excellent capacity retention and rate capability. To better understand the underlying reasons, DFT studies were performed to examine the surface effects on the composition, structural evolution, energetics, and Li mobility in amorphous Li_xSi alloys ($0.42 \leq x \leq 3.57$) [26]. When the Li content is sufficiently low, Li atoms tend to be
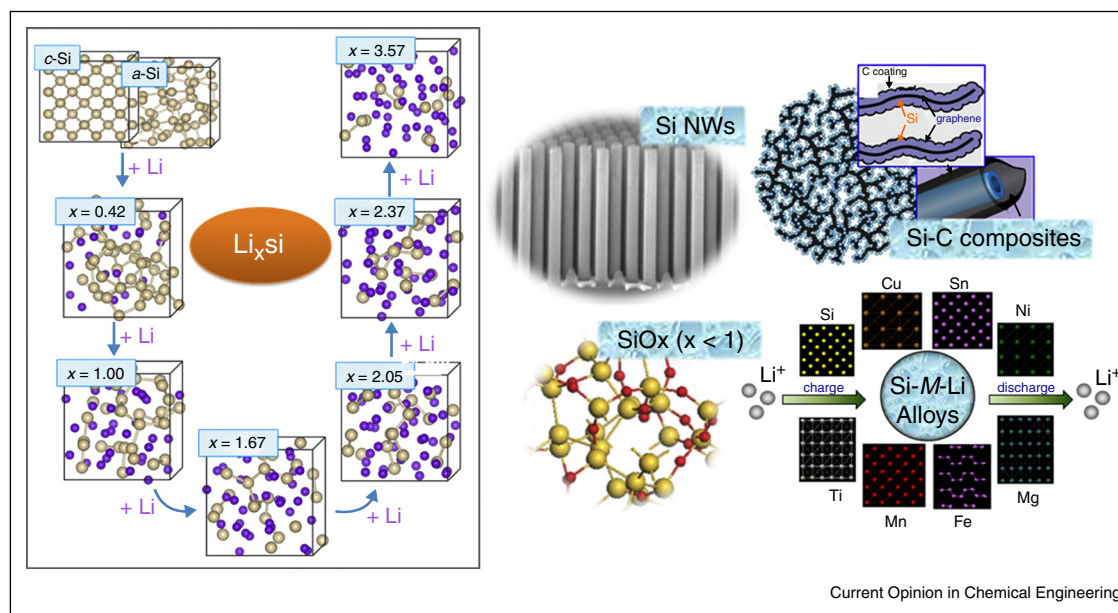
Various Si-based anode materials have been proposed and examined for next-generation Li-ion batteries. Upon Li incorporation, the bonding strengths among neighboring Si atoms are weakened, attributed to the transferred charge from Li. With increasing Li content, the Si lattice undergoes disintegration into low-connectivity clusters of various shapes, accompanied by significant volume expansion (~400%).

enriched in the surface layer for stabilization. As the Li content is further increased, the near-surface structure and alloy composition appears to be similar to that in the bulk, except for the reduction in Si–Si connectivity within the outermost surface layer. The surface effects are predicted to be very shallow and only extend to the first couple of atomic layers. Nonetheless, *ab initio* MD (AIMD) based on DFT highlights the improved Li mobility in the near-surface region. Additionally, Li mobility is predicted to be very sensitive to the alloy composition, and Li diffusivity is enhanced by orders of magnitude in the highly lithiated stage. ReaxFF MD simulations were also employed to demonstrate the lithiation of Si NWs, which occurs favorably along the (1 1 0) direction [27,28]. Facet-dependent lithiation behavior in crystalline Si was also examined using DFT calculations [29•]. It was shown that despite the anisotropic expansion during lithiation, the strain generated by the lithiation of the outer layers tends to further suppress Li diffusion [28].

Si suboxides SiO_x ($x < 2$) have also been recognized as a promising anode material for LIBs, especially when the O content is relatively low. It was reported that Si thin films with homogeneous O incorporation (≈ 13 at% O) in combination with surface oxidation exhibit an excellent capacity (≈ 2200 mAh/g) with nearly no capacity loss for the first 120 cycles, and 80% of the initial reversible capacity was retained after 300 cycles [20]. The lithiation mechanisms of partially oxidized Si has been examined using first-principles computational approaches [30–33]. From AIMD simulations, with lithiation amorphous $SiO_{1/3}$ was found to gradually disintegrate as Li atoms were accommodated by both Si and O atoms [30]. The AIMD study also predicts the formation of Li_6O complexes in which the four sp_3-hybridized orbitals of an isolated O^{2-} anion directed to the corners of a tetrahedron are surrounded by six Li cations each sitting over an edge. Li incorporation in the $SiO_{1/3}$ matrix was also predicted to be highly favorable with a capacity comparable to that of fully lithiated Si (Li:Si ratio ≈ 4). This computational study highlights the importance of controlling the Si:O ratio as well as O spatial distribution in order to tailor the desired lithiation properties. A later study varied the oxygen content over a much wider range and showed the volume expansion was inversely related to the O content in the SiO_x system [31]. It was also shown that very thin films of hydroxylated SiO_2 could be lithiated up to 3.48 Li per Si [32], however the volume expansion was not addressed due to the 2D nature of the material. SiCO was reported to exhibit similar lithiation properties to $SiO_{1/3}$, in that it does not form Li_2O, but exhibits less volume expansion even than SiO_2 [33]. Besides oxygen atom incorporation, the effects of other chemical impurities on Si lithiation have been also examined [34].

First-principles computational approaches have also been utilized to study the lithiation mechanisms and electrochemical properties of Si-based composites and coated Si NWs, with particular attention to the effects of interfaces [36–38]. As shown in Figure 2, a recent combined *in situ* characterization and first-principles study demonstrated an intriguing stagewise lithiation behavior in gold-coated Si nanowires (Au-SiNWs) in which Li atoms are incorporated preferentially in the Au shell while the AuSi interface tends to serve as a facile diffusion path along the nanowire axial direction, followed by the prompt lithiation of the Si core in the radial direction [35]. Despite the recent theoretical efforts, there is still lack of fundamental understanding of the lithiation of Si-based and C-based nanocomposites as anode materials in LIBs, warranting further investigations.

Anode/electrolyte interfaces: structural and chemical evolution

In order for the LIB to safely operate, the electrolyte must be stable under the reductive and oxidative conditions of the anode and cathode, respectively, or upon decomposition, a solid insulating layer can be formed to prevent further electron transfer. This layer at the electrode/electrolyte interface has been known as the solid electrolyte interphase (SEI) since it was discovered by Peled and co-workers at the Li metal surface [39]. Since then, a wide variety of compositions and structures have been

Figure 2

Current Opinion in Chemical Engineering
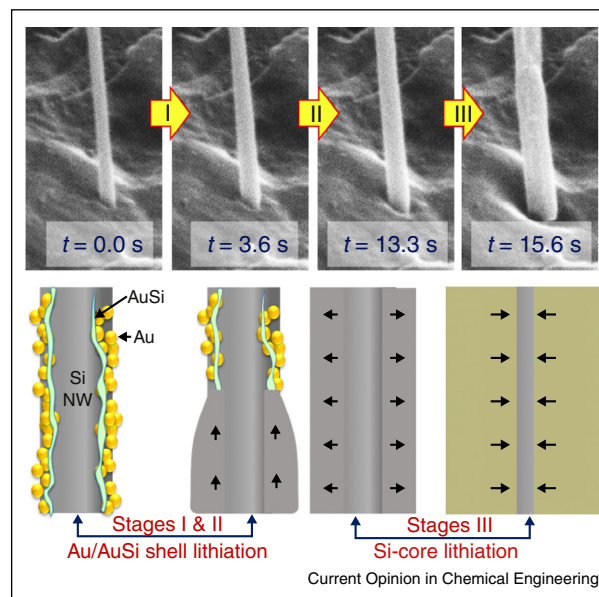
(Upper panels) Temporal microstructure evolution of an [1 1 1] Au-SiNW in direct contact with Li metal, demonstrating a stagewise lithiation behavior. (Lower panels) Proposed stagewise lithiation of an individual Au-SiNW. Stages I & II: axial lithiation of the Au shell with progressive and slow expansion while the AuSi interface layer may serve as a facile diffusion path. Stage III: radial lithiation of the Si-core with uniform and rapid expansion.
*Source*: Adapted from [35].

described in the literature, often in conflict with one another [40]. The ideal SEI layer should be thin, permit Li$^+$ ion transport at rates comparable to the electrolyte, and form with minimal electron transfer, thus minimizes capacity loss [41]. The electrolyte decomposition directly affects the capacity loss by determining the structure of the SEI and the requisite amount of sacrificial Li to form it. Additionally, further capacity losses may occur by decomposed electrolyte diffusing away from the anode and not contributing to the passivating film. Next, we will highlight how molecular simulations have been utilized in the study of these processes.

Computer simulations have been conducted across a spectrum of time and length scales to better understand how electrode surface, bulk electrolyte, and operating conditions affect the resultant SEI in order to better understand the origin of these variations. First-principles approaches based on DFT have been employed to screen electrolyte additives [42–44] that have lowest unoccupied molecular orbital (LUMO) energy levels lower than standard electrolyte molecules such as ethylene carbonate (EC) and dimethyl carbonate (DMC). Additives commonly used such as fluoroethylene carbonate (FEC) and vinylene carbonate (VC) [41] exhibit lower LUMO levels, suggesting that they would react before EC and thus could control SEI formation. However, such quick screening does not account for the effects of solvation and interface structure which would be essential in describing accurately the structural and chemical evolution at the interface. For example, vinylethylene carbonate (VEC) also has a LUMO energy lower than EC, but has been found to not form a stable SEI layer leading to large capacity fades [45].

AIMD simulations have been used to a great extent in an attempt to identify the reaction pathways involved in electrolyte decomposition at the anode. For EC at a graphitic carbon surface, it has been shown that two-electron pathways yielding either Li$_2$CO$_3$ or C$_2$H$_4$O$_2^{2-}$ tend to be preferred [46], despite the expectation of lithium ethylene dicarbonate (Li$_2$EDC) as the primary SEI component [41]. Later, based on rigorous first-principles calculations, Leung suggested that the electrolyte decomposition pathway may depend upon electron transfer rate (Figure 3), while demonstrating the possibility of Li$_2$EDC or lithium butylene dicarbonate (Li$_2$BDC) formation at slow electron transfer rates [47•]. A later AIMD study utilized thermodynamic integration techniques to establish an absolute potential scale to study the effects of voltage on electrochemical processes at a LiC$_6$/electrolyte interface [48]. Electrolyte decomposition in this study was found to be slower than the timescale utilized at potentials where SEI formation has been observed to begin experimentally.

The decomposition pathway of EC at a liquid Li metal anode has been also evaluated using AIMD simulations,

Figure 3
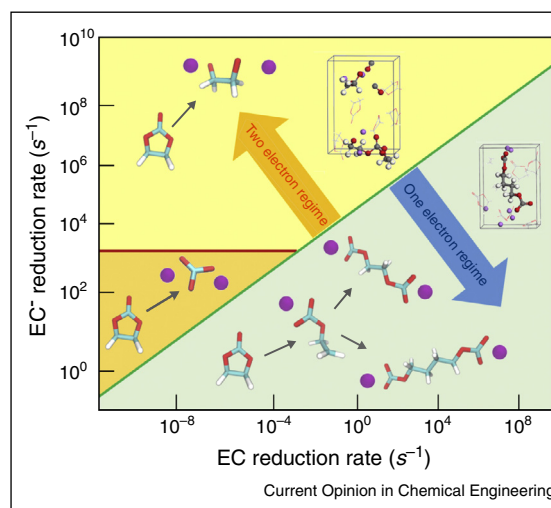
The decomposition products of EC are predicted at various electron transfer rates for both the initial electron received by EC as well as the second electron received.
Adapted from [47•].

showing a preference toward C$_2$H$_4$O$_2^{2-}$ formation. ReaxFF MD simulations have been performed to investigate decomposition of multiple electrolyte mixtures at a Li metal surface at various temperatures, demonstrating the formation of primarily Li$_2$O and Li$_2$CO$_3$ at the electrode/electrolyte interface [49].

Although there has been a push in the community to move toward Si anodes, the electrolyte decomposition at the Si surface has begun to be studied. The effects of lithiation and surface termination on the reduction of EC were studied [50]; the results have been found to significantly differ from decomposition on Si clusters with a single Li$^+$ adsorbed, as predicted by DFT studies [51•]. The reduction of FEC, a common additive, was also studied at Si surfaces [52]. Recently, the effects of other additives and co-solvents were studied as well [53]. The importance of explicit description of the Si/electrolyte interface was also highlighted by demonstrating the different reduction pathways for VC between in the electrolyte [54] and at the interface [52]. Alternatively, room temperature ionic liquid based electrolytes have also been shown to undergo similar decomposition pathways at a Si surface [55].

A large portion of the literature on SEI details the reductive decomposition of the electrolyte, however it is also important to study the structural evolution at the interface. Classical MD has been largely employed to examine the structural reorganization of organic electrolytes and SEI components near the electrode or SEI layer. For instance, Jorn et al. [56] studied the structure of the

electrode/SEI/electrolyte interface through analysis of density distributions of EC, Li^+ and PF_6^- in the presence and absence of the SEI under applied voltages. The interfacial structure and dynamics of SEI components, such as dilithium ethylene dicarbonate (Li_2EDC) and dilithium butylene dicarbonate (Li_2BDC), in contact with a mixed carbonate electrolyte, EC:DMC (3:7) doped with $LiPF_6$ were also evaluated using MD simulations with the many-body polarizable APPLE&P force field [57]. There was also an attempt to directly simulate electrolyte decomposition and SEI formation for different electrolytes and temperatures using ReaxFF MD simulations [49]. There still exists a gap in the literature currently in regards to the electrolyte structure near the electrode before its decomposition and how this structure changes, not only with electrolyte composition, but with structural and operating factors such as applied voltage, temperature, and electrode surface chemistry.

The electrolyte decomposition products must be insoluble in the bulk electrolyte and adsorb onto the electrode surface for the SEI to form. To gain additional understanding of this process, classical MD simulations have been utilized to show the relative solubilities of various products in EC, DMC, and a mixture of the two [58]. A more recent AIMD paper expresses that perhaps the desolvation and adsorption of decomposition products occurs through a collective process following aggregation near the electrode surface [59•]. In the case of intermediate species neither adsorbing, not reacting to completion, the resulting charge loss is partly responsible for coulombic inefficiency. To better understand this, the fate of radical intermediate species must be further studied. ReaxFF MD simulations have been also utilized to discern the fate of EC^- radical ions in solution at various concentrations. Li_2BDC was shown to be more favorable than Li_2EDC [60], despite the latter being a frequently observed SEI component. A recent DFT study also suggests that additives are critical to preventing further reactions beyond SEI formation [61].

Li^+ ion transport through the SEI layer greatly impacts the cell impedance and thus the overpotential required in charging. The SEI is often assumed to be crystalline in nature. Classical MD simulations have been performed to evaluate Li transport rates in organic crystalline Li_2EDC [62], while DFT calculations utilizing the nudged elastic band (NEB) method have been conducted to predict transport rates in often-observed organic and inorganic crystalline SEI components [63,64] as well as potential artificial SEI layers [65,66] that could possibly be formed to limit capacity loss. There is still a large disconnect between the decomposition of electrolyte and the formation of a crystalline SEI layer which needs to be further investigated. Using enhanced sampling techniques, such as the NEB method, the first-principles computational

approach can reliably predict relevant transport barriers responsible for the rate limitations in charging of LIBs.

Summary and outlook
Over the last decade, there has been significant progress in first-principles modeling of anode materials and anode/electrolyte interfaces by virtue of rapid advances in computing power and computational methodology. First-principles simulations have been extensively used to explore the lithiation mechanisms of carbon-based and silicon-based nanomaterials for LIB anodes as well as the behavior of reductive decomposition of carbonate-based solvent molecules during SEI formation on Li metal, graphite, or Si-based anodes. First-principles based force fields have also been developed for use in large-scale MD simulations to examine the lithiation/delithiation process in anode materials and the structural and chemical evolution at anode/electrolyte interfaces. Despite recent progress, there is still considerable lack of fundamental investigations on the formation and growth of SEI layers and the lithiation behavior of Si-based nanocomposites such as carbon scaffold Si nanoparticles and Si/metal oxide composites. First-principles based computer simulations will continuously play a key role in the detailed mechanistic study of electrode materials and electrode/electrolyte interfaces. The improved understanding gained from computational studies combined with experiments will be crucial for realizing next-generation electrical energy storage systems with long life at an affordable cost.

Acknowledgements

References and recommended reading
Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

1. Armand M, Tarascon J-M: **Building better batteries**. *Nature* 2008, **451**:652-657 http://dx.doi.org/10.1038/451652a.

2. Goodenough JB, Kim Y: **Challenges for rechargeable Li**
• **batteries**. *Chem Mater* 2010, **22**:587-603 http://dx.doi.org/10.1021/cm901452z.

3. Scrosati B, Garche J: **Lithium batteries: status, prospects and future**. *J Power Sources* 2010, **195**:2419-2430 http://dx.doi.org/10.1016/j.jpowsour.2009.11.048.

4. Thinius S, Islam MM, Heitjans P, Bredow T: **Theoretical study of Li migration in lithium–graphite intercalation compounds with dispersion-corrected DFT methods**. *J Phys Chem C* 2014, **118**:2273-2280 http://dx.doi.org/10.1021/jp408945j.

5. Raju M, Ganesh P, Kent PRC, van Duin ACT: **Reactive force field study of Li/C systems for electrical energy storage**. *J Chem Theory Comput* 2015, **11**:2156-2166 http://dx.doi.org/10.1021/ct501027v.

6. Perassi EM, Leiva EPM: **A theoretical model to determine intercalation entropy and enthalpy: application to lithium/graphite**. *Electrochem Commun* 2016, **65**:48-52 http://dx.doi.org/10.1016/j.elecom.2016.02.003.

7. Netz A, Huggins RA, Weppner W: **The formation and properties of amorphous silicon as negative electrode reactant in lithium systems**. *J Power Sources* 2003, **119–121**:95-100 http://dx.doi.org/10.1016/S0378-7753(03)00132-0.

8. Hatchard TD, Dahn JR: **In situ XRD and electrochemical study**
• **of the reaction of lithium with amorphous silicon**. *J Electrochem Soc* 2004, **151**:A838-A842 http://dx.doi.org/10.1149/1.1739217.

9. Gao B, Sinha S, Fleming L, Zhou O: **Alloy formation in nanostructured silicon**. *Adv Mater* 2001, **13**:816-819 doi:10.1002/1521-4095(200106)13:11<816::AID-ADMA816>3.0.CO;2-P.

10. Chan CK, Peng HL, Liu G, McIlwrath K, Zhang XF, Huggins RA,
• Cui Y: **High-performance lithium battery anodes using silicon nanowires**. *Nat Nanotechnol* 2008, **3**:31-35 http://dx.doi.org/10.1038/nnano.2007.411.

11. Wang CM, Li X, Wang Z, Xu W, Liu J, Gao F, Kovarik L, Zhang JG, Howe J, Burton DJ *et al.*: **In situ TEM investigation of congruent phase transition and structural evolution of nanostructured silicon/carbon anode for lithium ion batteries**. *Nano Lett* 2012, **12**:1624-1632 http://dx.doi.org/10.1021/nl204559u.

12. Howe JY, Burton DJ, Qi Y, Meyer HM, Nazri M, Nazri GA, Palmer AC, Lake PD: **Improving microstructure of silicon/carbon nanofiber composites as a Li battery anode**. *J Power Sources* 2013, **221**:455-461 http://dx.doi.org/10.1016/j.jpowsour.2012.08.026.

13. Wang JW, Liu XH, Zhao K, Palmer A, Patten E, Burton D, Mao SX, Suo Z, Huang JY: **Sandwich-lithiation and longitudinal crack in amorphous silicon coated on carbon nanofibers**. *ACS Nano* 2012, **6**:9158-9167 http://dx.doi.org/10.1021/nn3034343.

14. Beaulieu LY, Hewitt KC, Turner RL, Bonakdarpour A, Abdo AA, Christensen L, Eberman KW, Krause LJ, Dahn JR: **The electrochemical reaction of Li with amorphous Si–Sn alloys**. *J Electrochem Soc* 2003, **150**:A149 http://dx.doi.org/10.1149/1.1530151.

15. Fleischauer MD, Topple JM, Dahn JR: **Combinatorial investigations of Si–M (M = Cr + Ni, Fe, Mn) thin film negative electrode materials**. *Electrochem Solid-State Lett* 2005, **8**:A137 http://dx.doi.org/10.1149/1.1850395.

16. Kim T, Park S, Oh SM: **Solid-state NMR and electrochemical dilatometry study on Li⁺ uptake/extraction mechanism in SiO electrode**. *J Electrochem Soc* 2007, **154**:A1112 http://dx.doi.org/10.1149/1.2790282.

17. Hwa Y, Park CM, Sohn HJ: **Modified SiO as a high performance anode for Li-ion batteries**. *J Power Sources* 2013, **222**:129-134 http://dx.doi.org/10.1016/jjpowsour.2012.08.060.

18. Chang W-S, Park C-M, Kim J-H, Kim Y-U, Jeong G, Sohn H-J: **Quartz (SiO_2): a new energy storage anode material for Li-ion batteries**. *Energy Environ Sci* 2012, **5**:6895 http://dx.doi.org/10.1039/c2ee00003b.

19. Kim JH, Park CM, Kim H, Kim YJ, Sohn HJ: **Electrochemical behavior of SiO anode for Li secondary batteries**. *J Electroanal Chem* 2011, **661**:245-249 http://dx.doi.org/10.1016/j.jelechem.2011.08.010.

20. Abel PR, Lin YM, Celio H, Heller A, Mullins CB: **Improving the stability of nanostructured silicon thin film lithium-ion battery anodes through their controlled oxidation**. *ACS Nano* 2012, **6**:2506-2516 http://dx.doi.org/10.1021/nn204896n.

21. Kim H, Kweon KE, Chou C-Y, Ekerdt JG, Hwang GS: **On the nature and behavior of Li atoms in Si: a first principles study**. *J Phys Chem C* 2010, **114**:17942-17946 http://dx.doi.org/10.1021/jp104289x.

22. Kim H, Chou C, Ekerdt JG, Hwang GS: **Structure and properties of Li–Si alloys: a first-principles study**. *J Phys Chem C* 2011, **115**:2514-2521 http://dx.doi.org/10.1021/jp1083899.

23. Chou C-Y, Kim H, Hwang GS: **A comparative first-principles**
• **study of the structure, energetics, and properties of Li–M (M = Si, Ge, Sn) alloys**. *J Phys Chem C* 2011, **115**:20018-20026 http://dx.doi.org/10.1021/jp205484v.

24. Chou CY, Hwang GS: **On the origin of the significant difference in lithiation behavior between silicon and germanium**. *J Power Sources* 2014, **263**:252-258 http://dx.doi.org/10.1016/j.jpowsour.2014.04.011.

25. Wang Z, Su Q, Deng H, He W, Lin J, Fu YQ: **Modelling and simulation of electron-rich effect on Li diffusion in group IVA elements (Si, Ge and Sn) for Li ion batteries**. *J Mater Chem A* 2014, **2**:13976 http://dx.doi.org/10.1039/C4TA01614A.

26. Chou CY, Hwang GS: **Surface effects on the structure and lithium behavior in lithiated silicon: a first principles study**. *Surf Sci* 2013, **612**:16-23 http://dx.doi.org/10.1016/j.susc.2013.02.004.

27. Jung H, Lee M, Yeo BC, Lee KR, Han SS: **Atomistic observation of the lithiation and delithiation behaviors of silicon nanowires using reactive molecular dynamics simulations**. *J Phys Chem C* 2015, **119**:3447-3455 http://dx.doi.org/10.1021/jp5094756.

28. Ostadhossein A, Cubuk ED, Tritsaris GA, Kaxiras E, Zhang S, van Duin ACT: **Stress effects on the initial lithiation of crystalline silicon nanowires: reactive molecular dynamics simulations using ReaxFF**. *Phys Chem Chem Phys* 2015, **17**:3832-3840 http://dx.doi.org/10.1039/C4CP05198J.

29. Chan MKY, Wolverton C, Greeley JP: **First principles simulations**
• **of the electrochemical lithiation and delithiation of faceted crystalline silicon**. *J Am Chem Soc* 2012, **134**:14362-14374 http://dx.doi.org/10.1021/ja301766z.

30. Chou CY, Hwang GS: **Lithiation behavior of silicon-rich oxide (SiO1/3): a first-principles study**. *Chem Mater* 2013, **25**:3435-3440 http://dx.doi.org/10.1021/cm401303n.

31. Rahaman O, Mortazavi B, Rabczuk T: **A first-principles study on the effect of oxygen content on the structural and electronic properties of silicon suboxide as anode material for lithium ion batteries**. *J Power Sources* 2016, **307**:657-664 http://dx.doi.org/10.1016/j.jpowsour.2016.01.003.

32. Perez-Beltran S, Ramirez-Caballero GE, Balbuena PB: **First-principles calculations of lithiation of a hydroxylated surface of amorphous silicon dioxide**. *J Phys Chem C* 2015, **119**:16424-16431 http://dx.doi.org/10.1021/acs.jpcc.5b02992.

33. Liao N, Zheng B, Zhou H, Xue W: **Effect of carbon content on the structure and electronic properties of silicon oxycarbide anodes for lithium-ion batteries: a first-principles study**. *J Mater Chem A* 2015, **3**:5067-5071 http://dx.doi.org/10.1039/C4TA06932C.

34. Long BR, Chan MKY, Greeley JP, Gewirth AA: **Dopant modulated li insertion in Si for battery anodes: theory and experiment**. *J Phys Chem C* 2011, **115**:18916-18921 http://dx.doi.org/10.1021/jp2060602.

35. Chou CY, Seo JH, Tsai YH, Ahn JP, Paek E, Cho MH, Choi IS, Hwang GS: **Anomalous stagewise lithiation of gold-coated silicon nanowires: a combined in situ characterization and first-principles study**. *ACS Appl Mater Interfaces* 2015, **7**:16976-16983 http://dx.doi.org/10.1021/acsami.5b01930.

36. Stournara ME, Qi Y, Shenoy VB: **From ab initio calculations to multiscale design of Si/C core–shell particles for Li-ion anodes**. *Nano Lett* 2014, **14**:2140-2149 http://dx.doi.org/10.1021/nl500410g.

37. Chou C-Y, Hwang GS: **Role of interface in the lithiation of silicon-graphene composites: a first principles study**. *J Phys Chem C* 2013, **117**:9598-9604 http://dx.doi.org/10.1021/jp402368k.

38. Kim S-Y, Ostadhossein A, van Duin ACT, Xiao X, Gao H, Qi Y: **Self-generated concentration and modulus gradient coating design to protect Si nano-wire electrodes during lithiation**. *Phys Chem Chem Phys* 2016, **18**:3706-3715 http://dx.doi.org/10.1039/C5CP07219K.

39. Peled E: **The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems—the solid electrolyte interphase model**. *J Electrochem Soc* 1979, **126**:2047-2051 http://dx.doi.org/10.1149/1.2128859.

40. Aurbach D: **The study of electrolyte solutions based on ethylene and diethyl carbonates for rechargeable Li batteries**.

J Electrochem Soc 1995, **142**:2882 http://dx.doi.org/10.1149/1.2048659.

41. Xu K: **Nonaqueous liquid electrolytes for lithium-based rechargeable batteries**. Chem Rev 2004, **104**:4303-4418 http://dx.doi.org/10.1021/cr030203g.

42. Halls MD, Tasaki K: **High-throughput quantum chemistry and virtual screening for lithium ion battery electrolyte additives**. J Power Sources 2010, **195**:1472-1478 http://dx.doi.org/10.1016/j.jpowsour.2009.09.024.

43. Han Y-K, Moon Y, Lee K, Huh YS: **Computational screening of lactam molecules as solid electrolyte interphase forming additives in lithium-ion batteries**. Curr Appl Phys 2014, **14**:897-900 http://dx.doi.org/10.1016/j.cap.2014.04.006.

44. Cheng L, Assary RS, Qu X, Jain A, Ong SP, Rajput NN, Persson K, Curtiss LA: **Accelerating electrolyte discovery for energy storage with high-throughput screening**. J Phys Chem Lett 2015, **6**:283-291 http://dx.doi.org/10.1021/jz502319n.

45. Li W, Xiao A, Lucht BL, Smart MC, Ratnakumar BV: **Surface analysis of electrodes from cells containing electrolytes with stabilizing additives exposed to high temperature**. J Electrochem Soc 2008, **155**:A648 http://dx.doi.org/10.1149/1.2949507.

46. Leung K, Budzien JL: **Ab initio molecular dynamics simulations of the initial stages of solid–electrolyte interphase formation on lithium ion battery graphitic anodes**. Phys Chem Chem Phys 2010, **12**:6583 http://dx.doi.org/10.1039/b925853a.

47. Leung K: **Two-electron reduction of ethylene carbonate: a**
• **quantum chemistry re-examination of mechanisms**. Chem Phys Lett 2013, **568–569**:1-8 http://dx.doi.org/10.1016/j.cplett.2012.08.022.

48. Leung K, Tenney CM: **Toward first principles prediction of voltage dependences of electrolyte/electrolyte interfacial processes in lithium ion batteries**. J Phys Chem C 2013, **117**:24224-24235 http://dx.doi.org/10.1021/jp408974k.

49. Kim S-P, van Duin ACT, Shenoy VB: **Effect of electrolytes on the structure and evolution of the solid electrolyte interphase (SEI) in Li-ion batteries: a molecular dynamics study**. J Power Sources 2011, **196**:8590-8597 http://dx.doi.org/10.1016/j.jpowsour.2011.05.061.

50. Martinez De La Hoz JM, Leung K, Balbuena PB: **Reduction mechanisms of ethylene carbonate on si anodes of lithium-ion batteries: effects of degree of lithiation and nature of exposed surface**. ACS Appl Mater Interfaces 2013, **5**:13457-13465 http://dx.doi.org/10.1021/am404365r.

51. Ma Y, Balbuena PB: **DFT study of reduction mechanisms of**
• **ethylene carbonate and fluoroethylene carbonate on Li⁺-adsorbed Si clusters**. J Electrochem Soc 2014, **161**:E3097-E3109 http://dx.doi.org/10.1149/2.014408jes.

52. Martínez de la Hoz JM, Balbuena PB: **Reduction mechanisms of additives on Si anodes of Li-ion batteries**. Phys Chem Chem Phys 2014, **16**:17091 http://dx.doi.org/10.1039/C4CP01948B.

53. Martinez De La Hoz JM, Soto FA, Balbuena PB: **Effect of the electrolyte composition on SEI reactions at Si anodes of Li Ion batteries**. J Phys Chem C 2015, **119**:7060-7068 http://dx.doi.org/10.1021/acs.jpcc.5b01228.

54. Ushirogata K, Sodeyama K, Tateyama Y, Okuno Y: DFT-MD Study of Additive Effects On Reductive Decomposition of Carbonate-Based Solvent Toward Solid Electrolyte Interphase Formation. 2013:. 2013.

55. Piper DM, Evans T, Leung K, Watkins T, Olson J, Kim SC, Han SS, Bhat V, Oh KH, Buttry DA, Lee S-H: **Stable silicon–ionic liquid interface for next-generation lithium-ion batteries**. Nat Commun 2015, **6**:6230 http://dx.doi.org/10.1038/ncomms7230.

56. Jorn R, Kumar R, Abraham DP, Voth GA: **Atomistic modeling of the electrode–electrolyte interface in Li-ion energy storage systems: electrolyte structuring**. J Phys Chem C 2013, **117**:3747-3761 http://dx.doi.org/10.1021/jp3102282.

57. Borodin O, Bedrov D: **Interfacial structure and dynamics of the lithium alkyl dicarbonate SEI components in contact with the lithium battery electrolyte**. J Phys Chem C 2014, **118**:18362-18371 http://dx.doi.org/10.1021/jp504598n.

58. Tasaki K, Harris SJ: **Computational study on the solubility of lithium salts formed on lithium ion battery negative electrode in organic solvents**. J Phys Chem C 2010, **114**:8076-8083 http://dx.doi.org/10.1021/jp100013h.

59. Ushirogata K, Sodeyama K, Futera Z, Tateyama Y, Okuno Y: **Near-**
• **shore aggregation mechanism of electrolyte decomposition products to explain solid electrolyte interphase formation**. J Electrochem Soc 2015, **162**:A2670-A2678 http://dx.doi.org/10.1149/2.0301514jes.

60. Bedrov D, Smith GD, van Duin ACT: **Reactions of singly-reduced ethylene carbonate in lithium battery electrolytes: a molecular dynamics simulation study using the ReaxFF**. J Phys Chem A 2012, **116**:2978-2985 http://dx.doi.org/10.1021/jp210345b.

61. Soto FA, Ma Y, Martinez De La Hoz JM, Seminario JM, Balbuena PB: **Formation and growth mechanisms of solid-electrolyte interphase layers in rechargeable batteries**. Chem Mater 2015, **27**:7990-8000 http://dx.doi.org/10.1021/acs.chemmater.5b03358.

62. Borodin O, Zhuang GV, Ross PN, Xu K: **Molecular dynamics simulations and experimental study of lithium ion transport in dilithium ethylene dicarbonate**. J Phys Chem C 2013, **117**:7433-7444 http://dx.doi.org/10.1021/jp4000494.

63. Yildirim H, Kinaci A, Chan MKY, Greeley JP: **First-principles analysis of defect thermodynamics and ion transport in inorganic SEI compounds: LiF and NaF**. ACS Appl Mater Interfaces 2015, **7**:18985-18996 http://dx.doi.org/10.1021/acsami.5b02904.

64. Shi S, Lu P, Liu Z, Qi Y, Hector LG, Li H, Harris SJ: **Direct calculation of Li-ion transport in the solid electrolyte interphase**. J Am Chem Soc 2012, **134**:15476-15487 http://dx.doi.org/10.1021/ja305366r.

65. Hao S, Wolverton C: **Lithium transport in amorphous Al₂O₃ and AlF₃ for discovery of battery coatings**. J Phys Chem C 2013, **117**:8009-8013 http://dx.doi.org/10.1021/jp311982d.

66. Jung SC, Han YK: **How do Li atoms pass through the Al₂O₃ coating layer during lithiation in Li-ion batteries?** J Phys Chem Lett 2013, **4**:2681-2685 http://dx.doi.org/10.1021/jz401231e.