



Challenges for Na-ion Negative Electrodes

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Na-ion batteries have been proposed as candidates for replacing Li-ion batteries. In this paper we examine the viability of Na-ion negative electrode materials based on Na alloys or hard carbons in terms of volumetric energy density. Due to the increased size of the Na atom compared to the Li atom, Na alloys would lead to negative electrode materials with roughly half the volumetric energy density of their Li analogs. Volumetric energy densities obtainable with sodiated hard carbons would also be significantly less than those obtainable with lithiated graphite. These findings highlight the need of novel ideas for Na-ion negative electrodes. © 2011 The Electrochemical Society. [DOI: 10.1149/1.3607983] All rights reserved.

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Li-ion batteries dominate the portable electronics market and are currently seen as the only viable option in all-electric vehicles. Li-ion batteries are even considered for use in load-leveling applications on power grids. Li-ion technology is used because its high specific capacity and high voltage combine to yield an unmatched volumetric energy density.

Sony first commercialized the Li-ion battery in the early 1990's. The original chemistries for the negative and positive electrodes were based on hard carbon and LiCoO₂ respectively, although graphite quickly replaced hard carbon. Over the last twenty years three other major chemistries have been developed for the positive electrode: LiFePO₄, LiMn₂O₄, and transition metal substituted variants of LiCoO₂.¹ For the negative electrode, alloy-based materials are predicted to replace graphite, which remains the vastly dominant chemistry in commercial cells.²⁻⁴ Sony has offered a Sn-based negative electrode since 2005,⁵ and Panasonic has announced a Si-based negative electrode for 2013.⁶

When graphite is fully lithiated only 1/6 of a Li can be stored for every C atom. On the other hand in alloys up to approximately four Li atoms can be stored for every active metal (or semimetal).²⁻⁴ The advantage of alloy-based negative electrodes therefore lies in significantly increased volumetric and specific energy densities.

Na batteries were originally researched in tandem with Li batteries in the late 1970's and early 1980's.⁷⁻¹⁴ As the successes of Li batteries outnumbered those of Na batteries, the focus of the scientific community shifted away from Na. Na-ion batteries have therefore not been nearly as extensively studied as Li-ion batteries. In the last few years, a variety of factors have caused a renewal of interest in Na-ion batteries. The availability of Li in terms of a natural resource has been put into question with some claiming an eminent shortage¹⁵ if the automotive market embraces Li-ion batteries, while others claim either abundant,¹⁶ or sufficient reserves if large-scale recycling is implemented.¹⁷ Another motivation for the study of Na-ion batteries is that even though the field of Li-ion batteries has become increasingly competitive with more research effort, future directions for increasing the energy density through new chemistries remain unclear. Indeed, many of the commercial Li-ion cells with the highest energy densities remain based on graphite and LiCoO₂-derived cathodes.¹⁸ Our MIT group has used high-throughput computing to evaluate several tens of thousands of compounds.^{19,20} While some interesting novel compounds have emerged^{21,22} and are in the process of being developed, it is becoming clear that the options for much higher positive electrode energy density are becoming increasingly limited.

Most of the renewed academic interest in Na-ion batteries has focused on cathodes as the possibility of new Na-ion applicable crystal structures proves enticing.²³⁻²⁵ Recent computational studies of a wide variety of Na containing structures as positive electrodes for Na-ion batteries have shown them to operate on average approximately 0.4 V lower than their Li-ion analogs.²⁶ This will present a

challenge for Na-ion batteries as a lower positive electrode voltage leads to lower overall energy density. Assuming an excellent positive electrode is found for Na-ion batteries, a negative electrode will obviously also be required for Na-ion batteries to be commercially viable.

Few studies of candidate negative electrodes exist in the current scientific literature. Graphite cannot be used as a negative electrode as Na atoms will not intercalate between the carbon sheets.^{14,27,28} Na metal appears to form dendrites much like Li metal but its safety is further put into question by its low melting point of 97.7°C compared to 180.5°C for Li. Hard carbons have been identified as possible negative electrode materials, where Na atoms adsorb onto the surfaces of nanoscopic pores throughout the hard carbon particles. Na alloys as negative electrode materials have yet to be extensively studied. If the evolution of Li-ion and Na-ion batteries follow a similar path, Na alloys are likely to become a field of growing interest for Na-ion batteries.

This paper will seek to answer the question of whether hard carbons and Na alloys will lead to Na-ion batteries that are viable competitors to Li-ion batteries in terms of volumetric energy density. Much of the analysis uses insights developed for Li-ion batteries and is inspired in large part by Ref. 29.

Theory

Volumetric energy density.—Several metrics are used to qualify electrode materials. The most common is the specific capacity, typically with units of mAh/g, because it is the easiest to measure. However it can be convincingly argued that volumetric energy density (Wh/cc) is the most relevant metric for most Li-ion battery applications. If one considers Na-ion batteries as a candidate substitute, similar considerations should apply.

Firstly, the most widespread application of Li-ion batteries is portable electronics where the volume is the limiting factor. The weight of the battery could vary considerably without a significant impact to the user experience, but the volume must typically be as small as possible. Even in electric vehicles the volume is arguably the limiting factor. In power grid applications cost may trump volume considerations, however volumetric energy density is also an important driver for cost reduction as cells have a large fixed cost (electrolyte, separator, current collector, casing, etc. . .) and a higher volumetric energy density electrode implies that fewer cells have to be fabricated to achieve a total energy storage capability.

Secondly, it is the energy, not the charge, which is stored in the battery that will dictate the amount of work a battery can accomplish. One therefore seeks to maximize the voltage window of the battery by maximizing and minimizing the positive and negative electrode potentials respectively. In order to compare negative electrodes one can compare them by using a hypothetical positive electrode of constant voltage.

One can therefore conclude that the volumetric energy density should be one of the first criteria considered when evaluating an

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electrode and this paper will focus on the volumetric energy density (Wh/cc) obtainable with hard carbons and Na alloys.

The volumetric energy density (\tilde{U}) is defined as

$$\tilde{U} = \frac{F}{v(x_f)} \int_0^{x_f} (V_{(+)}(x) - V_{(-)}(x)) dx \quad [1]$$

where F is Faraday's constant (26.802 Ah/mol), V is the voltage of the positive (+) and negative (-) electrodes, x is the number of moles of Na (or Li) per mole of host alloy, and v is the density of the sodiated (or lithiated) active material in cc per mole of host alloy.

Binder limitations.—The large amount of Li that can be alloyed on a per atom basis in alloy negative electrode materials causes massive changes in volume.⁴ For example, the full lithiation of Sn and Si leads to volume expansions of 260 and 280% respectively. Several studies have shown that this massive volume expansion can lead to poor cycle life. Capacity fade can be caused by pulverization of the active particles³⁰ or degradation of the electrode coating.³¹ The capacity fade of alloy based negative electrodes is very sensitive to the choice of binder.^{31,32} A good binder must ideally maintain adhesion of the electrode to the current collector, maintain ionic contact, and facilitate the formation of a stable interface with the electrolyte.

In general, the volume expansion of the negative electrode must be limited in order to yield long term stable cycling. Currently, the best way of limiting the volume expansion is by diluting the active material with inactive material,²⁹ leading to more stable cycling but also to lower specific and volumetric capacities. This is the approach taken in the commercialized Sn-based material where Co acts mainly as an inactive diluent.⁵

Universal expansion curve.—Experimental and theoretical studies have shown that the volume occupied by Li atoms in Li-M alloy negative electrodes is essentially independent of M and of lithiation level, and constant at 14.8 Å³ (8.9 ml/mol). Based on this fact, Obrovac et al. derived a “universal expansion curve” for the design of alloy negative electrodes²⁹ allowing the energy density (\tilde{U}) to be calculated based on the volume occupied by Li (k), the average voltage of the full cell (V_{avg}) and final volume expansion (ξ_f) of the active/inactive negative electrode

$$\tilde{U} = \frac{F}{k} V_{\text{avg}} \left(\frac{\xi_f}{1 + \xi_f} \right) \quad [2]$$

where F is Faraday's constant. This powerful equation allows one to assess the merit of a negative electrode using readily available information. This approach can also be applied to the design of Na-based negative electrodes. All that is needed is the volume occupied by Na atoms and the average voltages of Na negative electrodes. Few experimental studies of Na alloy negative electrodes exist in the literature and significant effort would be required to test several different Na alloys as negative electrodes. However, the ability to calculate accurate average lithiation voltages and lattice parameters using density functional theory has been established for years and can readily be applied to this problem.^{19,33}

The voltages for Na alloys are therefore obtained computationally and a hypothetical positive electrode with a constant voltage of 3.75 vs. Li or Na metal is used to calculate the full cell voltage. The hypothetical 3.75 V positive electrode is used when considering both Li and Na alloys. Recent theoretical studies have shown that Na substitution into all the major Li-ion positive electrode structure classes leads to potentials that are on average 0.4 V lower.²⁶ This would represent an additional drop in volumetric energy density at the full cell level, which is not considered in this paper. The possible shrinking of the Na-based positive electrode during desodiation is also not considered in this paper. Na positive electrodes shrink to a greater extent than their Li counterparts, which are often found to

vary very little in volume during delithiation. The total volume of a full cell is typically at its greatest in the charged state (lithiated/sodiated negative electrode) since the alkali atoms occupy greater volumes because they are not fully ionized. If one designs cell packaging to accommodate the volume of the full cell in its charged state, the volume of the desodiated or delithiated positive electrode should be considered. The difference in volumes between desodiated positive electrodes and their delithiated counterparts are computationally found to be small. The possible greater shrinking of Na positive electrodes should therefore not affect the current conclusions.

Computational Methods

Density functional theory (DFT) calculations in the general gradient approximation (GGA) were performed. Projector augmented wave (PAW) (Ref. 34) pseudopotentials included in the Vienna Ab-initio Simulation Package (VASP 5.2.2) were used with the Perdew-Burke-Ernzerhof (PBE) functional.³⁵

Spin-polarized total energy calculations and structure relaxations were performed with VASP using a 500 eV energy cut-off and appropriate k -point meshes to obtain a convergence of better than 10 meV per formula unit. Structural relaxations were performed to a tolerance of 2×10^{-4} eV/atom in the total energy. Voltage curves are calculated using standard methods.^{36,37}

Results and Discussion

Figure 1 shows the sodiation voltage curves obtained from the DFT total energies for Si, Ge, Sn, and Pb. Calculations were performed using known crystal structures obtained from the Inorganic Crystal Structure Database (ICSD).³⁸ Overall, the average sodiation voltages are on average 0.15 V lower than calculated average lithiation voltages. A recent computational study of Na positive electrodes showed their voltages to be consistently lower by approximately 0.4 V.²⁶ Experimental sodiation data in the literature were only found for Pb (Ref. 12) and are included in Fig. 1. Rather good agreement is found between the experimental and theoretical Pb sodiation voltages. The Na₃Pb₂ phase was not included in the calculations as the Na sites in the crystal structure have not yet been experimentally defined.

The experimental volumes of the crystal structures used for the sodiation voltage curves were used to calculate the volume occupied by Na in Na-M alloys. Figure 2 shows that structure volumes increase linearly with Na content confirming Na occupies a constant volume, which is calculated from the slope as being $k_{\text{Na}} = 30.3 \text{ \AA}^3$. Na atoms therefore occupy approximately twice the volume of

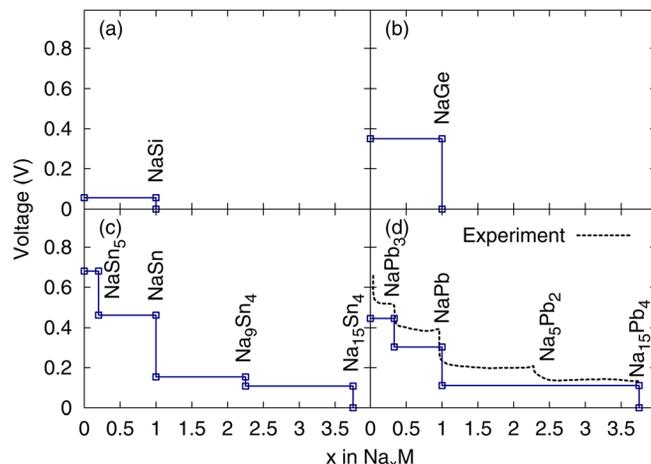


Figure 1. (Color online) Na-M voltage curves calculated using DFT and known Na-M crystal structures. (a) M = Si, (b) M = Ge, (c) M = Sn, and (d) M = Pb. Experimental data for (d) are adapted from Ref. 12.

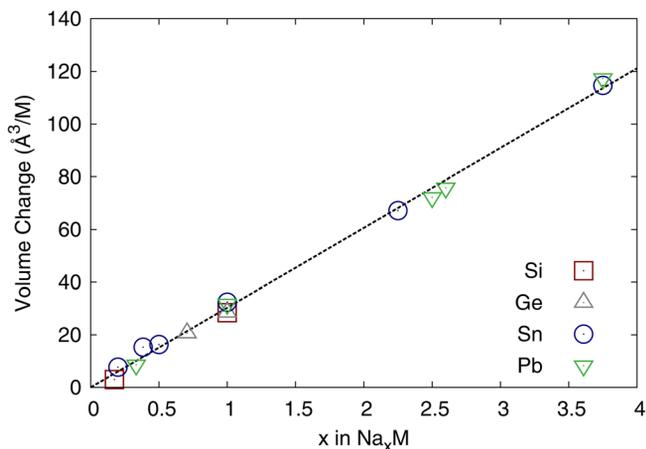


Figure 2. (Color online) The volume change ($\text{\AA}^3/\text{M}$) compared to elemental M for known crystalline Na-M alloys ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) increases linearly as a function of Na content. A linear fit shows each Na atom occupies 30.3 \AA^3 on average, independent of M, or Na content.

Li atoms ($k_{\text{Li}} = 14.8 \text{ \AA}^3$) when used in alloy negative electrodes. This is roughly in agreement with a comparison of the elemental volumes of Li ($21.6 \text{ \AA}^3/\text{atom}$) and Na ($39.4 \text{ \AA}^3/\text{atom}$).

Using the Na volume and the average sodiation voltages the volumetric energy density of Si, Ge, Sn, and Pb can now be plotted using Eq. 2. Figure 3 shows the volumetric energy density of Si, Ge, Sn, and Pb as a function of volume expansion. The volume expansion is in turn a linear function of sodium content. Figure 3 shows that if a Si negative electrode is used with a binder able to sustain a 100% volume expansion, 2.7 Wh/cc can be achieved with Na. This should be contrasted with the 4.7 Wh/cc obtainable with Li.²⁹

Hard carbons have been reported as high capacity carbon-based negative electrodes for Na-ion batteries³⁹ and their merit in terms of volumetric energy density should be evaluated. Hard carbons have very large surface areas and sodiation occurs through the adsorption of Na atoms onto the surfaces of nanoscopic pores throughout the hard carbon particles, which leads to low volume expansion. As a best-case scenario, we assume a zero volume expansion. The volumetric energy density (1.7 Wh/cc) can then be calculated from the experimental hard carbon density³⁹ ($\sim 1.5 \text{ g/cc}$), capacity²⁷ ($\sim 340 \text{ mAh/g}$) and average voltage (0.33 V , obtained by digitizing and integrating the delithiation curve in Fig. 6b of Ref. 27).^{27,39,40} The volumetric energy density obtained with hard carbons is included in

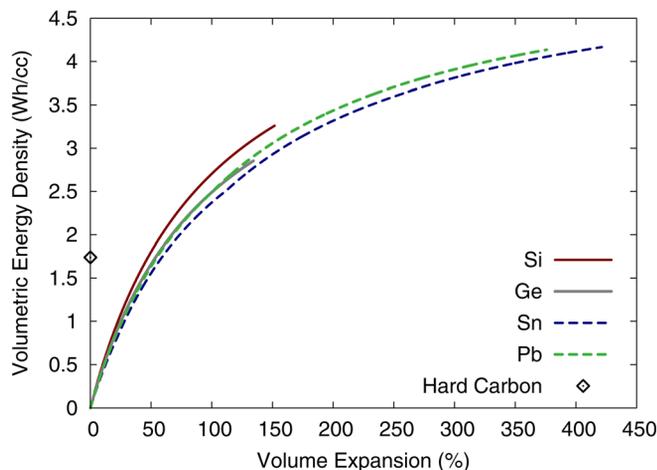


Figure 3. (Color online) Volumetric energy density and volume expansion obtained from the corresponding sodiation voltage curves of Fig. 1, and Eq. 1. Ge and Pb curves overlap significantly.

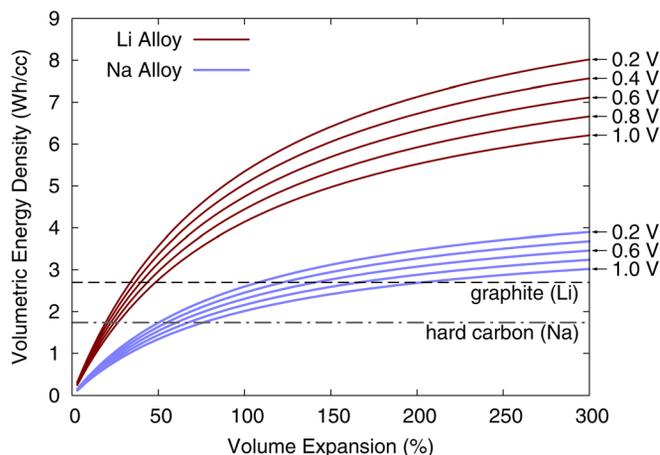


Figure 4. (Color online) Universal expansion curves for Li and Na alloys. The volumetric energy densities of lithiated graphite and sodiated hard carbon are included for ease of comparison but are not a function of the volume expansion axis.

Figure 3 for ease of comparison. As with Li, the carbon-based approach leads to a considerably lower volumetric energy density than the alloy-based approach. The volumetric energy density of hard carbons with Na (1.7 Wh/cc) should be contrasted with the volumetric energy of graphite with Li (2.7 Wh/cc).

Figure 4 shows the universal expansion curves of Li and Na-based alloy negative electrodes. The volumetric energy densities of lithiated graphite and sodiated hard carbons for Na are also included for ease of comparison, although the volume expansion axis does not apply to them. These curves can be used to evaluate the volumetric energy density obtained from an active/inactive composite where the active fraction is fully lithiated or sodiated. The reader is encouraged to read Ref. 29 for more details.

The large difference in volumetric energy density between Li and Na negative electrodes is a direct consequence of the greater volume occupied by the Na atom as can be seen from Eq. 2. Therefore, if all parameters except k are kept identical, the volumetric energy density of a sodiated alloy negative electrode will be $k_{\text{Li}}/k_{\text{Na}} = 49\%$ of a lithiated one.

Figure 4 also shows that even if a discovery allowed acceptable cycling of Na alloys at 300% volume expansion, these would still have a lower volumetric energy density than what is obtained with 50–100% volume expansion in Li alloys. An example of a Li alloy demonstrating good cycling is the $\text{Sn}_{30}\text{Co}_{30}\text{C}_{40}$ attrited material of Ferguson et al., which has a capacity of roughly 450 mAh/g for 100 cycles⁴¹ and a density of 6.7 g/ml .⁴² Assuming a constant Li volume of 8.9 ml/mol , this represents a 100% volume expansion of the alloy. Acceptable cycling with 100% volume expansions in Li alloys is therefore *already* achievable with current technologies and it is unlikely that solutions to volume expansion challenges would be specific to Na-alloys and not applicable to Li-alloys.

In the current market, the cost of Li represents less than 3% of the production cost of a full commercial Li-ion battery.⁴³ Even if Na was considerably less expensive because of its widespread availability, it is worthwhile to question whether the savings in cost would be lost when taking into account the costs associated with having a negative electrode with a significantly lower volumetric energy density.

Conclusion and Outlook

There is growing interest in Na-ion batteries as a candidate replacement for Li-ion batteries. A viable Na-ion battery will require a negative electrode yielding sufficient volumetric energy density. In this paper we have shown that Na-ion negative electrodes based on

current strategies and technologies are unlikely to be able to compete with their Li-ion analogs in terms of volumetric energy density. Hence, focus should be on novel ideas for the negative electrode side, or on positive electrode materials which have substantially higher energy densities than the current Li-ion positive electrodes in order to overcome the limitations on the negative electrode side.

These findings highlight the need for new strategies and approaches for Na-based energy storage technologies. Indeed, an attempt to mimic current Li-ion technologies is unlikely to lead to a viable competitor to Li-ion batteries.

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