Journal of Alloys and Compounds 688 (2016) 158–163

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Advantages of Ge anode for Na-ion batteries: Ge vs. Si and Sn

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ARTICLE INFO

Article history:
Received 17 May 2016
Received in revised form
15 July 2016
Accepted 18 July 2016
Available online 19 July 2016

Keywords:
Na-ion battery
Energy storage materials
Amorphization
Electrochemical reactions
Ionic conduction
Molecular dynamics simulations

ABSTRACT

The sodiation properties of alloy-type anode materials (Si, Ge, and Sn) have been evaluated in terms of electrochemical energy storage using first-principles molecular dynamics calculations. We report that Ge can deliver reasonably good performance in all aspects of sodium storage capability, mechanical stability, and ion conductivity, when compared with Si and Sn. The Ge anode: (1) has a strong thermodynamic driving force for sodiation that is comparable to that of Sn and much stronger than that of Si, (2) exhibits moderate volume expansion and bulk modulus upon sodiation that are superior to those of Sn, and (3) allows fast Na ion conductivity that is comparable to that of Sn and is faster by three orders of magnitude than that of Si. Our study suggests that among the group 14 elements, Ge is fairly promising as an anode material for Na-ion batteries.

1. Introduction

Li-ion batteries (LIBs) are extensively utilized in everyday life, serving as power sources for a wide variety of mobile electronics [1–3]. The market demand for LIBs has been increasing dramatically because of their use in portable electronic devices as well as in large-scale products, such as energy storage systems (ESSs), electric vehicles (EVs), hybrid electric vehicles (HEVs), and plug-in hybrid electric vehicles (PHEVs) [1–3]. However, natural Li resources are limited in their availability by geographical constraints and shortages [4,5]. Na-ion batteries (NIBs) have been gaining interest lately among battery researchers as a possible alternative to LIBs owing to the natural abundance of Na, its low toxicity, and its redox chemistry based on monovalency. The merit of a very low cost has led to the consideration of the NIB as a particularly promising alternative to the LIBs, especially with large-scale grid storage systems [4–13].

The chemical similarity of Na to Li allows the existing Li technology to make a substantial contribution toward the discovery of suitable electrode materials for NIBs. Efforts have been devoted to materials that are structurally similar to those used for electrodes in LIBs [6], however, no suitable anode materials have yet been identified for NIBs. For example, the most commonly used anode material for LIBs is graphite, but this fails to intercalate Na effectively [14–17]. Thus, improvements in the anode materials are urgently needed for the optimization of Na technology.

Alloy-type anode materials, such as group 14 elements, have been extensively studied in the LIBs because of their considerably high theoretical capacities [3,18–21]. Therefore, these elements can also be used to improve the capacity of NIBs. Of the group 14 elements, Si has low activity as an anode material for NIBs [4,22–26]. A reversible capacity of 279 mAh g^{-1} was recently achieved using Si nanoparticles [27], but Si is still considered a poor choice for a Na storage material. By contrast, Sn delivers initial capacities of 856–878 mAh g^{-1} [24,28,29], which are comparable to the theoretical capacity of 878 mAh g^{-1} [30], and it forms crystalline $Na_{3.75}Sn$ at the end of sodiation [24,28,29]. However, this occurs in parallel with a volume expansion of up to 420% for $Na_{3.75}Sn$, which essentially precludes the utilization of this high capacity. During electrochemical cycling, this enormous volume change due to the sodiation of Sn leads to a continuous pulverization of the electrode material and then a rapid deterioration of cyclability. A reversible capacity of 339 mAh g^{-1} for a nano-sized Sn electrode was reported, but this decreased to 145 mAh g^{-1} after 400 cycles [31]. The rapid capacity fading during charging/discharging due to the huge volume change (420%) has severely hindered the applicability of Sn in practical NIBs.

On the other hand, Ge, which is lighter than Sn but heavier than

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http://dx.doi.org/10.1016/j.jallcom.2016.07.201

Si, is a promising Na battery anode material. Experimental tests have demonstrated practical reversible capacities and better capacity retention for Ge than for Si or Sn anodes. Baggetto et al. [32] experimentally demonstrated that Ge thin film electrodes electrochemically react with Na with a reversible capacity around 350 mAh g^{-1}. Abel et al. [12] obtained reversible storage of Na in nanocolumnar Ge electrodes with an initial capacity of 430 mAh g^{-1} and reported retention of 88% of this capacity after 100 cycles. Kohandehghan et al. [33] demonstrated that amorphization of Ge nanowires and thin films by a single lithiation–delithiation cycle led to improvements in the Na capacity (412–450 mAh g^{-1}), the rate capability, and the cycling stability. Recently, Xiaotang et al. [13] reported that amorphous Ge nanowire can be sodiated to a final sodiated phase of $Na_{1.6}Ge$ with a maximum capacity of 590 mAh g^{-1}. This report is in excellent harmony with our computational result [30], where the sodiation of amorphous Ge can lead to the formation of $Na_{1.56}Ge$ that can provide a theoretical capacity of 576 mAh g^{-1}.

We mention that electrochemical performance also can be affected by the size and morphology of alloy-type anode materials (extrinsic factors) [12,13,27,32–38]. Although these factors should be optimized for practical application of NIBs, main focus of this work is the intrinsic factors, influenced by the electronic and structural properties of alloy materials.

In the present work, we investigate the average voltage curves, coordination numbers, radial distribution functions, Bader charge populations, diffusivity, and bulk modulus of sodiated Ge. Our aim is to extend our previous study on the formation energies and volume expansions of sodiated Ge [30] and to compare these values with those of sodiated Si and Sn. The greatest advantage of Ge in terms of battery performance is its ability to allow fast Na ion diffusivity in Ge materials, which is comparable to that in Sn materials, faster by three orders of magnitude than that in Si materials, and even faster by one order of magnitude than Li ion diffusivity in Si, and eventually leads to a high rate capability. The fully sodiated Ge also exhibits a higher bulk modulus when compared with the corresponding Sn, implying a higher resistance against structural damage during sodiation and a better capacity retention in Ge than in Sn. Our diffusivities and bulk moduli of Na_xM (M = Si, Ge, and Sn) were determined at the fully sodiated states and are distinguishable from previous calculations of Chou et al. [39] for a particular composition (Na: M = 1: 1).

2. Computational details

The density functional theory (DFT) calculations were carried out based on the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functionals [40] for electron–electron interactions and the projector augmented wave (PAW) method [41] for electron–ion interactions, as implemented in the Vienna ab initio simulation package (VASP) [42,43]. We employed a plane wave basis with a kinetic energy of 400 eV. We used valence electron configurations of $2p^6 3s^1$ for Na, $3s^2 3p^2$ for Si, $4s^2 4p^2$ for Ge, and $5s^2 5p^2$ for Sn. The amorphous Na_xM bulk structures were represented by a periodic cubic supercell, which includes $40 \times x$ Na and 40 M atoms (M = Si, Ge, and Sn). Brillouin zone integrations were done with a $2 \times 2 \times 2$ *k*-point mesh. The mass densities of amorphous Ge and Sn were calculated to be 5.40 and 6.94 g cm^{-3}, respectively, which agree with the experimental values of 5.32 and 7.36 g cm^{-3}, respectively. We performed ab initio molecular dynamics (MD) calculations to generate the amorphous structures. We have integrated the equations of motion using the Verlet algorithm with a time step of 1 fs. The velocity rescaling and canonical ensemble using a Nosé–Hoover thermostat were applied to control the temperature. The amorphous structures were generated by rapidly cooling the liquid phase. The Bader charges [44], radial distribution functions (RDFs), and coordination numbers (CNs) were examined for the equilibrium Na_xGe and Na_xSn structures; i.e., the room-temperature simulation structures during the final MD step in the procedure for constructing the amorphous phases. A $1 \times 1 \times 1$ *k*-point mesh was employed to save the computation time during the MD simulations. The RDF and CN results were acquired using the RINGS code [45]. Detailed procedures for constructing the amorphous structures can be found in our previous studies [30,46–48].

3. Results and discussion

The energetically most stable phases of amorphous Na_xSi, Na_xGe, and Na_xSn alloys are $Na_{0.76}Si$, $Na_{1.56}Ge$, and $Na_{3.89}Sn$, respectively, which have formation energies of −0.15, −0.43, and −0.50 eV, respectively, and the corresponding specific capacities of 725, 576, and 878 mAh g^{-1}, respectively [30]. The larger formation energies of sodiated Ge and Sn (−0.43 and −0.50 eV, respectively) than of sodiated Si (−0.15 eV) indicate that the Ge and Sn sodiation is energetically more feasible than that of Si. The experimental capacities of Ge (590 mAh g^{-1} [33]) and Sn (~860 mAh g^{-1} [24,28,29]) are comparable to the theoretical capacities of 576 and 878 mAh g^{-1}, respectively, but the experimental capacity of Si (279 mAh g^{-1} [27]) is far less than the theoretical capacity of 725 mAh g^{-1}. The low experimental capacity of Si, corresponding to only 40% of the theoretical value, would be associated with the smallest formation energy of sodiated Si. The very low reactivity of Si toward sodiation could deliver a relatively weak thermodynamic driving force for the sodiation of Si. By contrast, the sodiation of Ge is as energetically favorable as that of Sn, implying a strong thermodynamic driving force for the sodiation of Ge.

The average voltage curves during sodiation of amorphous Ge and Sn are obtained using the calculated total energies for amorphous Na_xGe and Na_xSn alloys, respectively, and are shown in Fig. 1. The X-ray diffraction experiments conducted by Baggetto et al. [32] revealed that the starting amorphous Ge anode remains amorphous at full sodiation, with no evidence for the formation of a crystalline phase, and the potential profile of Ge during sodiation exhibited a single wide plateau. Overall, the calculated voltage curves of the amorphous Na_xGe and Na_xSn alloys, shown in Fig. 1a and b, respectively, lie in between the experimental charge–discharge profiles [49], indicating that our calculations reasonably describe the thermodynamic equilibrium voltage during sodiation.

The volume expansion ratios of Si, Ge, and Sn at full sodiation are 114% ($Na_{0.76}Si$), 205% ($Na_{1.56}Ge$), and 451% ($Na_{3.89}Sn$), respectively [30]. The volume expansion ratio of Sn is in reasonable agreement with the experimental value of 424% for $Na_{3.75}Sn$ [5] and is considerably larger than the volume expansion ratio of Ge and Si, due to the much larger Na uptake by Sn. The Na ions also occupy more spaces in Sn than in Si and Ge. The calculated volumes occupied by one Na atom in amorphous Na–M alloys are 27.7, 29.2, and 32.4 Å^3 for Si, Ge, and Sn, respectively. The severe volume changes for Sn during cycling could cause the pulverization of electrode and rapid capacity fading. The volume expansion ratio (205%) of Ge is considerably smaller than that (451%) of Sn, possibly leading to relatively good mechanical stability and capacity retention of a Ge anode.

The Na insertion/extraction kinetics shows a strong association with the rate capability during cycling. The computed diffusivities of Na in Si, Ge, and Sn are listed in Table 1. The mean-square displacements (MSD) of Na atoms were calculated from the MD simulations for 10 ps at $T = 1200$, 1600, 2000, and 2400 K, and the self-