Journal of Power Sources 275 (2015) 32–37

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Carbon-free and two-dimensional cathode structure based on silicene for lithium–oxygen batteries: A first-principles calculation

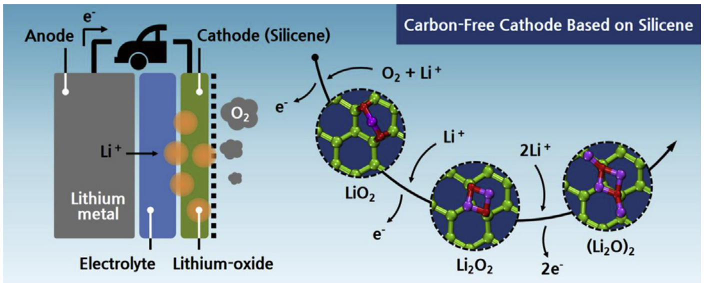
Yubin Hwang, Kyung-Han Yun, Yong-Chae Chung*

Department of Materials Science and Engineering, Hanyang University, Seoul 133-791, Republic of Korea

HIGHLIGHTS

- Carbon-free cathode based on silicene is first proposed for Li–O_2 batteries.
- ORR/OER can occur on the pristine form of silicene without any defects.
- Strong adsorption of ORR intermediates is caused by ionic bonding between O and Si.
- Structural stabilization of silicene also affect the adsorption of ORR intermediates.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 September 2014
Received in revised form
4 November 2014
Accepted 4 November 2014
Available online 5 November 2014

Keywords:
Lithium–oxygen batteries
Cathode
Silicene
Oxygen reduction reaction
Electrochemistry
Density functional theory

ABSTRACT

The lithium–oxygen (Li–O_2) battery is one of the most promising technologies for energy storage due to its extremely high-energy density. However, the design still faces many challenges for practical use including the decomposition of cathodes, which are typically composed of carbon-based materials. In this study, a carbon-free and two-dimensional cathode structure based on silicene is first proposed for Li–O_2 batteries using density functional theory calculations. In contrast to graphene, oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) can occur on the pristine form of silicene without any defect sites. In addition, it was found that reactions on silicene strongly correlate with strong adsorptions of the ORR intermediates, which are caused not only by ionic bonding between the oxygen atoms in the ORR intermediates and silicene but also by the structural stabilization of silicene. Theoretical observations demonstrate the great potential of silicene as a carbon-free cathode structure for Li–O_2 batteries and provide further insights for designing a new cathode material architecture based on two-dimensional structured materials.

1. Introduction

The exponential growth of environmental concerns and climate change have led to calls for "low-carbon" impact not only in industrial fields but also in other areas of scientific research. One such field that is undergoing the biggest change is the automotive industry. However, there are many scientific and technical challenges to replace existing vehicles, which have engines using petroleum-based fuels, with electric vehicles (EVs) with lower-emission (potentially zero-emission) greenhouse gases. In the past decade, lithium ion batteries have been regarded as the dominant power source for EVs. However, they still do not provide enough energy density (387 W h kg^{-1}) [1,2] compared to existing fossil fuels, i.e., gasoline and diesel (theoretically 12,200 W h kg^{-1} and 13,762 W h kg^{-1}, respectively) [3]. This difference is a major obstacle to the commercialization of EVs. Hence, lithium–oxygen batteries have attracted great attention as a new energy storage system due to their potential to provide energy density that is

---

* Corresponding author.
E-mail address: yongchae@hanyang.ac.kr (Y.-C. Chung).

http://dx.doi.org/10.1016/j.jpowsour.2014.11.016

several times higher (theoretically 11,680 W h kg^{-1}) than lithium ion batteries [1,2,4–9].

However, there are still many obstacles limiting the practical application of Li–O_2 batteries, including poor rate capability, low round trip efficiency, and a short cycle life (typically below 100 cycles) [8,10–12]. All of these obstacles are mainly caused by the sluggish kinetics of the oxygen reduction reactions (ORR) (during discharging) and the oxygen evolution reactions (OER) (during charging) at the oxygen diffusion cathodes, which are typically based on various carbon materials, i.e., porous carbons, carbon nanotubes, and graphene-based materials [2,8,13]. Carbon-based structures have a large surface area to offer more active sites for both ORR and OER as well as a large pore volume to store the discharge products of Li_2O_2 or Li_2O. These properties make them widely used to form cathodes for non-aqueous Li–O_2 batteries [14–21]. However, during the ORR/OER, cathode structures containing carbon atoms cause decomposition of the cathodes themselves and the electrolytes into highly irreversible products of a Li_2CO_3-like species, resulting in limitation of the rechargeability and progressive corrosion of the Li–O_2 batteries [22–25]. To avoid generating these products, carbon-free materials have been suggested to form the cathode structures for Li–O_2 batteries [26–29].

In the present study, the ORR/OER mechanisms on silicene as a carbon-free cathode structure for Li–O_2 batteries are investigated to reveal the potential for replacing existing carbon-based materials. Silicene has emerged to replace graphene as an alternative material with novel properties resulting from its two-dimensional honeycomb structure such as its high surface area, massless Dirac fermion, high thermal conductivity, high electrical conductivity, and a zero-gap semiconductor [30–35]; however, unlike graphene, silicene has a buckled structure consisting of silicon atoms instead of carbon atoms, and a more reactive surface than graphene due to its partial sp^3-like lattice [30,35,36]. Herein, density functional theory (DFT) calculations show for the first time that silicene itself has great potential for cathode materials without any metal or oxide catalysts in the Li–O_2 batteries. Moreover, it is revealed that pristine silicene could provide active sites for the ORR/OER, unlike the case of graphene, on which the ORR/OER occur at defective sites such as the vacancy, edge, and doped-atoms. The computational results also provide further insight into the fundamental understanding of the reaction mechanism, including the adsorption behavior of the ORR intermediates, on carbon-free and two-dimensional cathode structures for Li–O_2 batteries.

2. Computational methods

Spin-polarized DFT calculations were carried out using the projector augmented-wave (PAW) method [37], as implemented in the Vienna ab initio Simulation Package (VASP) code [38,39]. The Perdew-Burke-Ernzerhof (PBE) within the generalized gradient approximation (GGA) was adopted to examine the electronic exchange-correlation function of the interacting electrons [40]. A model of the pristine silicene sheet was created by taking a 4 × 4 supercell of silicene, which was chosen to be large enough to make the intermolecular interactions negligible. In order to compare with the adsorption strength of the ORR intermediates on graphene, a model of the pristine graphene sheet was prepared by taking a 6 × 6 supercell of graphene, which corresponds to that of silicene. The sheets were placed in a vacuum spacing of 15 Å in the direction normal to the sheet, which was sufficient to avoid interlayer interaction between the two adjacent periodic images. The optimized lattice constant of the silicene and graphene unit cell were found to be 3.868 Å and 2.469 Å respectively, which were in good agreement with previous theoretical work [35,41].

The kinetic cutoff energy for the plane-wave basis expansion was chosen to be 520 eV, and the Brillouin zone (BZ) was sampled using a 4 × 4 × 1 and a 3 × 3 × 1 k-point mesh generated by the Γ-centered Monkhorst-Pack scheme [42] for the silicene and graphene supercell, respectively. BZ integrations were performed with the Methfessel-Paxton smearing method with the broadening width equal to 0.1 eV [43]. The energy convergence criteria in the self-consistent field was set to 10^{-5} eV, and a conjugate gradient approach was used with a maximum force tolerance of 0.02 eV/Å for structural optimization. For reliable results, convergence tests were performed with respect to the supercell size, lattice constant, vacuum spacing, cutoff energy, and k-point sampling.

In this study, a free energy diagram was achieved by the most stable adsorption configuration of the ORR intermediates among all the possible configurations. The free energies of the ORR intermediates in the electrochemical reaction pathways were calculated using Eq. (1):

$$\Delta G = \Delta E^{\text{tot}} + \Delta E^{\text{ZPE}} - T\Delta S \tag{1}$$

where ΔE^{tot}, ΔE^{ZPE}, and ΔS denote the total energy change directly obtained from the DFT calculations, the change in the zero-point energies, and the change in the entropy at $T = 298.15$ K, respectively. The effect of a bias can be applied by shifting ΔG by $-neU$, where n is the number of electrons transferred, e is the elementary positive charge, and U is the applied bias. The values of ΔE^{ZPE} and ΔS of the ORR intermediates were calculated from the vibrational frequencies obtained by using a widely used method for DFT calculations. The adsorption energies of the ORR intermediates on silicene were calculated according to Eq. (2):

$$E_{\text{ads}} = -\left[E_{\text{Li}_x\text{O}_2/\text{silicene}} - E_{\text{Li}_x\text{O}_2} - E_{\text{silicene}}\right] \tag{2}$$

where $E_{\text{Li}_x\text{O}_2/\text{silicene}}$, $E_{\text{Li}_x\text{O}_2}$, and E_{silicene} represent the calculated total energy of silicene with the adsorbed ORR intermediate, the free ORR intermediate, and the relaxed silicene sheet, respectively. A Bader analysis was used to compute the charge transfer values [44,45].

3. Results and discussion

3.1. Free energy diagram for the ORR/OER

The ORR mechanisms at the cathodes in non-aqueous Li–O_2 batteries have been investigated experimentally and theoretically, and the following two ORR mechanisms have been suggested [6,7,46–51]:

$$2\left(\text{Li}^{+}+\text{e}^{-}\right) + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2\left(\text{a two}-\text{electron pathway}\right) \tag{3}$$

$$4\left(\text{Li}^{+}+\text{e}^{-}\right) + \text{O}_2 \rightarrow 2\left(\text{Li}_2\text{O}\right)\ \left(\text{a four}-\text{electron pathway}\right) \tag{4}$$

In the case of Eq. (3), O_2 is directly reduced to Li_2O_2, while in the case of Eq. (4), O_2 is reduced to Li_2O with the formation of the Li_2O_2 intermediate [8,12,52]. In general, it is known that the pathway is significantly influenced by how easily the O_2 molecule is dissociated at the surface in cathode or catalyst materials [53]. It has been reported that the ORR mechanism at Pt, Pd, PtCo, and PdCu, which has been known for the best catalysts and readily dissociates the O_2 molecules at the surfaces, occurs through a four-electron pathway (Eq. (4)) [54,55]. Özçelik and Ciraci suggested that silicene promotes the dissociation of the O_2 molecules at the surface as metal