An ab initio study for electrochemistry: Superconductor layer FeAs as a novel anode material for lithium ion batteries

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Abstract: A potential application of Fe-based layers (FeAs, FeSe) as a new promising anode material was proposed in the fields of second batteries by systematic first-principles calculations. The calculation results indicate that those conventional superconductor layers, such as FeAs, can deliver a theoretical capacity of 1 044 mAh/g, three times higher than that of the graphite-type anode. Further dynamic investigation suggests that Li/FeAs experiences a conversion reaction forming Li_3As and Fe through a two-step reaction in the first cycle. In the following cycles, Li-ion reversibly intercalates into arsenic at 0.77 V or deintercalates from Li_3As at 1.16 V, which is similar to the lithiation/de-lithiation mechanism of silicon anode materials. Based on their high energy density and good dynamic mechanism, these superconductor layers are thought to be a complex functional electrode candidates for future large-energy batteries systems.

Key words: superconductor layer; lithium-ion battery; density functional theory; relative energy

从头计算确定 FeAs 超导层能够作为锂离子电池的新型负极材料

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摘要: 通过第一性原理计算发现这些传统的铁基超导层状材料(FeAs)不仅十分适合作为锂离子电池负极, 同时它们还具有1 044 mAh/g 的高理论容量, 几乎是传统石墨负极材料的三倍容量. 计算证实, 在第一次充电过程中, Li/FeAs 将首先通过两步转换反应形成最终产物 Li_3As 和 Fe. 在接下来的放-充电过程中则主要通过 As 和锂离子之间的合金化反应来实现电池的可持续充放电, 其电化学平台分别为 0.77 V 和 1.66 V,

这与硅负极材料的合金化反应机理十分类似. 鉴于这类材料高的能量密度及好的动力学性能, 我们有理由相信铁基超导层状材料可以作为一种复杂功能化的电极材料而应用于未来的电池储能系统.

关键词: 超导层; 锂离子电池; 密度泛函理论; 相对能量

0 Introduction

Lithium-ion batteries (LIBs), have been widely used in portable electronics, and are now expanding into the fields of high-energy power supply and grid-energy storage systems[1-5]. However, conventional anode materials, such as commercial graphite, still cannot satisfy the new requirements of high energy/power density due to their relatively low specific capacity (e. g., 372 mAh/g for graphite)[6]. Therefore, much effort has been devoted to developing new anode materials. For instance, silicon (Si) is thought to be an ideal anode material because of its high theoretical capacity of 3 590 mAh/g at room temperature[7-9]. However, the extreme volume change ($\sim$ 370% assuming final alloy of $Li_{15}Si_4$) during electrochemical processes results in the structural pulverization and electrical disconnection between active materials and the current collector, leading to serious capacity fading[10]. Meanwhile, the research on many other anode candidate materials, such as Sn, GeO_2, MoS_2, etc., was also carried out during the past decades, but until now, none has been applied to commercial facilities[11-14]. Thus, searching for new anode materials with high capacity and good cycle stability is still a great challenge.

The iron-based superconductor, whose fundamental block is FeAs or FeSe layer, has been a hot research spot due to its high T_c (55 K) since it was first discovered in 2008[15]. Among the many candidates in Fe-based superconductors, two types of $Li_x(FeAs)_{1-x}$ are worth noting because of their possible capacity for storing Li-ions. One is FeAs with composition $x = 0$, and the other is "111" type of LiFeAs with composition $x = 1/2$. Fig. 1 shows the $2 \times 2 \times 2$ supercell crystal structure of FeAs and LiFeAs, respectively. It can

be found that the FeAs compound is of the MnP-type structure with orthorhombic $Pnma$ space group, and the "111" types of compounds are layered structures, which are similar to commercial α-$NaFeO_2$ cathode materials[16-18]. Furthermore, as we know, the tetrahedral coordinated Fe_2As_2 blocks are sandwiched by two charge reservoir layers, which play important roles in metallic conduction and superconductivity. Most importantly, the charge reservoir layers are alkali metal layers in the "111" system. Taking their similar crystalline structure into consideration, it is meaningful to explore their potential electrochemical performance as novel electrodes for Li/Na-ion batteries.

Here, we explore this new potential application of the Fe-based superconductor layer as a promising anode for Li-ion batteries by the first principles calculations. The most possible dynamic mechanism is also proposed by simulating the electrochemical intermediates during the charge-discharge process. It is indicated that the entire electrochemical process can be divided into two steps for FeAs. Firstly, Li_3As and Fe are formed in the first cycle by a conversion reaction similar to the electrochemical process of transition metal oxides. Secondly, Li-ions reversibly intercalate into arsenic or deintercalate from Li_3As in the following cycles, as silicon's electrochemical process. Based on this mechanism, this new anode candidate can provide a theoretical capacity as high as 1044 mAh/g. Finally, we also simulate the electrochemical energy profile on the charge-discharge cycle model of the Li/FeAs cells using the density functional theory (DFT). The appropriate charge/discharge plateau shows that this superconductor material is a promising anode candidate for Li-ion batteries.

1 Computational methods

All calculations were performed using the plane wave DFT code VASP (Vienna ab initio Simulation Package)[19]. We applied the projector augmented wave (PAW)[20-22] to describe the electronic wave functions，where the $3p^6 4s^1 3d^7$ and $4s^2 4p^3$ are treaded as the valence for Fe and As atoms，respectively. The local density approximation with the generalized gradient approximation of PBE functions was adopted for the exchange correlation term[23]. A $9 \times 9 \times 9$ Monkhorst-Pack k-point grid[24] and a 400 eV energy cutoff of the plane wave function were adopted to guarantee calculation accuracy. According to several first principles calculations for the Fe-based superconductor[16-17]，the van der Waals interaction was not taken into consideration in our work. We constructed different structures according to different stoichiometries x in the compounds $Li_x (FeAs)_{1-x}$. The initial lattice parameters and positions of atoms were taken from the experimental data of LiFeAs[25] and $KFe_2 As_2$[26]. In order to obtain the optimal structures and the lowest energies，we have optimized the geometry，volume and internal position parameters for all structures. The convergence of the total energy was set to be less than 1×10^{-3} eV.

According to the Nernst's equation[27]，the open circuit voltage (OCV) can be calculated by using the Gibbs free energy change ΔG depending on the equation $OCV = -\Delta G / zF$，where z is the charge transported by an ion in the electrolyte and F is the Faraday constant. The Gibbs free energy can be derived from the calculation of the enthalpy $H(T)$ and entropy $S(T)$ by Eq. (1)~(4)[28].

$$E(T) = \frac{h}{2} \int_0^{\omega_{max}} \omega \cos\left(\frac{\hbar\omega}{2K_B T}\right) g(\omega) \, d\omega \qquad (1)$$

$$S(T) =$$

$$K_B \int_0^{\omega_{max}} \left[\frac{\hbar\omega}{2K_B T} \cos\left(\frac{\hbar\omega}{2K_B T}\right) - \ln\left(2\sin\frac{\hbar\omega}{2K_B T}\right) \right] g(\omega) \, d\omega \qquad (2)$$

$$H(T) = E_T + E(T) + PV \qquad (3)$$

$$G(T) = H(T) - TS(T) \qquad (4)$$

Where E_T is the total energy ground state，$E(T)$ represents the internal energy，$\hbar$ is the Planck constant，$g(\omega)$ is the phonon density of states，$\omega(\omega_{max})$ is the phonon frequence in the lattice，and K_B is the Boltzman constant. The phonon density of states can be calculated using the force constants，which can be supported by VASP[29]. Then，a phonopy program was used. In the whole calculation，the small volume change was neglected in the solid phase reaction under constant pressure.

2 Results and discussion

2.1 Crystallographic structure of iron arsenide compounds

It is well known that FeAs，LiFeAs，$Li_2 FeAs$ and $LiFe_2 As_2$，typical iron arsenide compounds，have a similar chemical formula. The number of lithium atoms is the only difference. However，we found that their main framework structures are also different，not only for the Li-Fe bonds，but also for the Fe-As bonds，even though both of them have the layer structure. Furthermore，the coordination environment of Fe and As for these compounds is also completely different，as shown in Fig. 1. Our further theoretical calculations also confirmed this. The detailed lattice parameters of FeAs，LiFeAs，$Li_2 FeAs$ and $LiFe_2 As_2$ are listed in Tab. 1，which coincide with previous experimental results[16,28]. The structural distinction from the
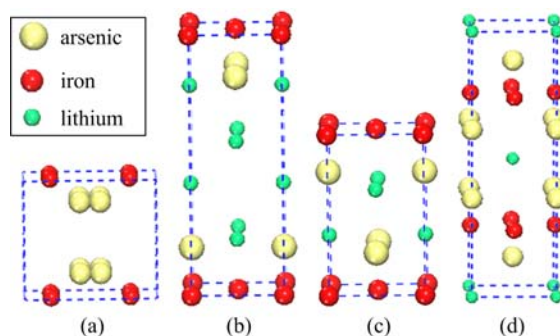

Fig. 1 Crystal structures of (a) FeAs，(b) $Li_2 FeAs$，
(c) LiFeAs and (d) $LiFe_2 As_2$

conventional transition metal oxides, such as $LiCoO_2$, demonstrates that there may be other lithiation mechanisms for iron arsenide compounds rather than the intercalated/de-intercalated mechanism[30-32]. Considering their similarity to Fe_2O_3, we proposed that this is a typical conversion reaction for these iron arsenide compounds. Thus, we calculated the structure of several possible intermediates, such as Fe and Li_3As. The lattice comparison with experimental parameters are listed in Tab. 1. It can be found that the calculated results agree with previous experimental data, indicating that the theoretical data is reasonable. In the next section, the possible mechanism of this system is discussed by introducing their formation energies.

Tab. 1   Calculated structure parameters along with the experimental data

formula	space group	lattice parameters/Å					
		calculation			experiment		
		a	b	c	a	b	c
Fe	$Im3m$	2.840	2.840	2.840	2.886	2.886	2.886
FeAs	$Pnam$	5.440	6.025	3.371	5.313	6.963	3.373
LiFeAs	$p4/nmms$	3.771	3.771	6.357	3.772	3.772	6.358
Li_2FeAs	$p4/nmms$	3.650	3.650	10.32	—	—	—
$LiFe_2As_2$	$14/mmm$	3.851	3.851	10.01	—	—	—
Li_3As	$p63/mmc$	4.450	4.450	7.880	4.374	3.374	7.813

2.2   Dynamic mechanism.

From the above structural analysis, it is easy to observe that both of FeAs and LiFeAs are the most important products during this electrochemical process, no matter which reaction mechanism they belong to. Even though it seems that the possible dynamic mechanism of those superconductors is the same as the intercalation/de-intercalation mechanism of transition metal oxides. However, our further calculated results show that it prefers a more complex reaction combined with conversion and alloying reaction rather than a simple intercalated/de-intercalated reaction as expected. Actually, in a typical conversion reaction, the material of the initial structure changes completely during the redox

reaction between lithium ion and transition metal compounds. In order to understand its reaction mechanism, the formation energies of several possible intermediates and final products were examined by DFT calculations. The formation energy is defined by $E_f = E_{Li_x(FeAs)_{1-x}} - xE_{Li} - (1-x)E_{FeAs}$, where $E_{Li_x(FeAs)_{1-x}}$ are the total energies of $Li_x(FeAs)_{1-x}$, E_{FeAs} and E_{Li} are the energies of FeAs compounds and Li[28]. The calculated potential energy diagram on the charge-discharge cycle model of the Li/FeAs cell is presented in Fig. 2. For the full discharge reaction (Eq. (5)) under enough Li-ion concentration, the energetically favorable final products are Li_3As and Fe metal. Accordingly, a two-step reaction mechanism (Eqs. (5) and (6)) for the first cycle can be proposed. First FeAs is lithiated forming intermediate LiFeAs, then this intermediate continues lithiation finally generating Li_3As and Fe. In the following cycles, Li_3As is responsible for providing reversible capacity through alloying reaction. Meanwhile, Fe does not participate in the electrochemical reaction, but can play an important role in restricting volume change of As during cycling, just like Eq. (7). This can improve the cycling performance effectively, ensuring the long cycle life of this new anode. On the other hand, its theoretical capacity can reach 1044 mAh/g based on Eq. (6) ~ (7), suggesting that this novel material can also provide a high capacity at the same time.
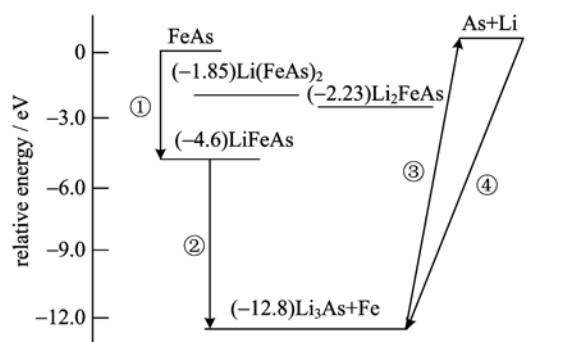

Fig. 2   Charge-discharge potential energy diagram of Li/FeAs

Tab. 2　Calculated open-circuit voltage（OCV）for each reaction of Li/FeAs cells at 298. 15 K

	reaction	equation	OCV/V	
			calculation	experiment
discharge	$FeAs + Li^+ + e^- \longrightarrow LiFeAs$	（5）	0. 47	0. 5～0. 4
	$LiFeAs + 2Li^+ + 2e^- \longrightarrow Li_3As + Fe$	（6）	0. 38	0. 4
	$As + 3L^+ + 3e^- \longrightarrow Li_3As$	（7）	0. 77	0. 8～0. 6
charge	$Li_3As \longrightarrow As + 3Li^+ + 3e^-$	（8）	1. 16	1. 1

Eqs. (5) and （6）show the two-step reaction of the first cycle，and Eq. （7）shows the subsequent cycles.

$$FeAs + Li^+ + e^- \longrightarrow LiFeAs \qquad (5)$$

$$LiFeAs + 2Li^+ + 2e^- \longrightarrow Li_3As + Fe \qquad (6)$$

$$As + 3L^+ + 3e^- \longrightarrow Li_3As \qquad (7)$$
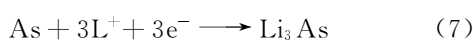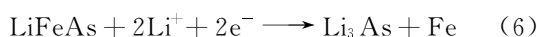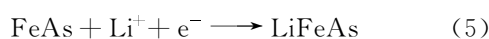
Based on the proposed conversion mechanism，we found that three Li-ions can be reacted during the entire charge/discharge process，suggesting that a higher theoretical capacity can be achieved. This means that these iron arsenide compounds can be treated as a promising anode candidate for lithium ion batteries on the aspect of energy density. Nevertheless，the redox potential for the lithium removal cannot be ignored when evaluating an electrode material for LIBs. Thus，we calculated the open-circuit voltage of every step as described in the part of calculation methods. The detailed open-circuit voltage is listed in Tab. 2. In the first cycle，there are two discharge potential plateaus appearing at 0. 47 V and 0. 4 V，because of its complex conversion reaction. After experiencing this unique conversion reaction and forming the final product with Li_3As，the lithiation mechanism changes to the alloying mechanism，which is the same as the silicon anode. The first charge potential is estimated to be 1. 16 V according to Eq. （8）. And the subsequent discharge plateaus are calculated to be 0. 77 V. The calculated values are very close to the experimental results，as observed in Chen's work[33]. Their experimental work demonstrated that there are also four plateaus for this layered structure[33]. We have reasons to believe that our proposed mechanism is in accordance with the electrochemical reaction.

3　Conclusion

As a novel energy material of LIBs，FeAs is of great research value. In this work，we utilized the DFT calculations to simulate the electrochemical energy profile on the charge-discharge cycle model of Li/FeAs. For the full discharge reaction，the final products are Li_3As and iron mental under enough Li-ion concentration. In the first cycle，it is a two-step reaction. In the subsequent cycles，Li-ion reversibly intercalates into arsenic or deintercalate from Li_3As. Fe does not participate in the electrochemical reaction，which is consistent with the experimental data.

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