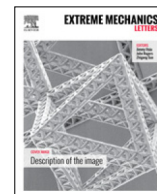




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Interfacial adhesion energy of lithium-ion battery electrodes

Yan Wang^{a,1}, Yujie Pu^{b,1}, Zengsheng Ma^{b,*}, Yong Pan^b, Chang Q. Sun^{c,*}^a School of Information and Electronic Engineering, Hunan University of Science and Technology, Xiangtan 411201, Hunan, China^b National-Provincial Laboratory of Special Function Thin Film Materials, and School of Materials Science and Engineering, Xiangtan University, Xiangtan 411105, Hunan, China^c NOVITAS, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

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ABSTRACT

Interfacial stability of electrode materials is crucial to the internal resistance and electrochemical performance of the lithium-ion batteries. However, determination of the cohesive energy at the heterogeneous interface remains yet a great challenge. Here, we report an approach and outcomes of quantifying the heterogeneous interfacial adhesion strength of the lithium-ion battery electrodes using the combination of the bond-order-length-strength (BOLS) correlation theory and X-ray photoelectron spectroscopy (XPS). Results revealed that the core-bond electrons of Ge/Si, Cu/Sn, Si/C and Ge/C alloys undergo quantum entrapment, while the C 1s electrons in Si/C and Ge/C alloys undergo polarization. Most strikingly, besides the interfacial adhesion energies, we are able to gain the local bond energy, energy density, atomic cohesive energy, and free energy at the interfaces. The presented approach and outcomes not only clarify the origin of the energetic behavior of the hetero-junction interface but also provide with reliable strategies for designing alloy electrodes with desired functions.

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1. Introduction

As the promising back-up power source, rechargeable lithium-ion batteries (LIBs) are the key components of electric vehicles, portable electronic devices, implantable medical devices, power tools, and future hybrid electric vehicles due to their superior energy density, high capacity, and variable discharge rate [1]. Owing to the rapid advancement of electronic technologies, large amount of efforts have been made on improvement of power levels of the LIBs by developing new electrode materials or designing new structures to meet the compatibility of higher power density, long cycle life, excellent rate capability performance and environmental compatibility. So far, many electrodes composed of a single active material have been investigated, such as graphite [2], silicon nanowires [3,4], germanium nanowires [5], etc. However, these materials have limitations in practical applications. For instance, graphite has already been widely commercialized for LIBs, but its low specific capacity ($\sim 372 \text{ mAh g}^{-1}$) may hardly meet the demands of higher power density [6]. Although Si has been deemed as one of most potential alternatives due to its highest

known theoretical capacity ($\sim 4200 \text{ mAh g}^{-1}$) and harmlessness to the environment, a huge volume deformation ($> 300\%$) during lithium insertion and extraction may damage seriously its cycle life [7–9], which induces a high stress on the silicon particles and causes pulverization and rapid capacity fading [3,10–12]. Mechanical degradation under cyclic charging and discharging has been the one of the most important bottlenecks for the developments of lithium ion batteries [13,14]. Ge and Sn faced the same problem as Si [15,16].

Fortunately, the core-shell structured composite electrodes by alloying reactions of elemental materials can improve the electrochemical performance to some extent compared with elemental material anodes, which promises greatly as future generation of battery electrodes [17]. Up to now, considerable attempts have been focused on the core-shell structured electrodes, such as Si/C nanocomposite [18], Ge/C nanocomposite [19], Sn/C nanoparticles [20], etc. However, a contact loss issue of the heterogeneous interface between elemental active materials seriously affects the capacity and electrochemical performances of LIBs [21], which was caused by large deformation and volume expansion when the battery is at working that is subject to Li-ion insertion and extraction inducing depressed conductivity, and eventually limits their applications [22]. Stable interface structure can ensure good contacting, which can provide a reliable situation to the ionic and electronic transmission [14]. Therefore, to seek and distinguish an electrode

* Corresponding authors.

E-mail addresses: zsm@xtu.edu.cn (Z. Ma), ECQSun@ntu.edu.sg (C.Q. Sun).¹ These authors contributed equally to this project.

for LIBs with a better electrochemical performance, it is essential to quantify the interfacial adhesion energy of the alloying electrode for the interfacial stability of hetero-coordinated structures and active materials-current collector.

At the present, there are many experimental and theoretical methods to obtain the heterogeneous interface energy quantitatively or semi-quantitatively, such as the peel test [23,24], pressurized blister test [25], microscratch test [26,27], and superlayer test [28]. These methods are reasonable enough to flat surface albeit accuracy, however, it is difficult to quantify the interfacial adhesion energy of electrode materials for LIBs, because their scale is too small and the interface is too rough to do the test. What is more, it is impossible to tear the interface alloy whose adhesion strength is stronger than yield strength of the constituent materials.

Conversely, computational techniques such as *ab initio* calculations using Peierls-Nabarro model [29] and molecular dynamics [30] can be used to calculate the interfacial energy. The simulation results are very helpful in revealing the deformation mechanism for the ideal crystal structures. Hence, with the aid of X-ray photoemission spectroscopy (XPS), we seek for effective means to quantify the interfacial adhesion energy of electrode materials.

This work aims to show that we are able to extract quantitative information, such as atomic cohesive energy and binding energy density, to characterize the interfacial energy at the interface of different active materials or the interface between the active material and current collector by formulating and analyzing XPS measurements on the framework of bond order-length-strength (BOLS) correlation theory [31,32]. We emphasize that bond order distortion and bond nature alteration induced bond relaxation and the associated quantum entrapment and polarization dictate the performance of the hetero-interface of electrode materials for LIBs.

2. Principles

2.1. Interface BOLS correlation theory

The core idea of the extended BOLS theory is that bonds between hetero-coordinated atoms relax spontaneously in both length and energy due to bond order distortion and bond nature alteration [33,34]. Consequently, localization, densification, entrapment or polarization of charge, energy, and mass will occur immediately to the interface region when the hetero-interface bond forms. The driving force for the bond deformation arises from the localization and densification of interface electrons. The energy stored at the interface layer perturbs the Hamiltonian and hence varies the related physical properties, such as the core level shift, the binding strength and electron distribution in real and energy spaces. The influence of hetero-coordinated interface on the core level shift enables us to obtain quantitatively its energetic information.

The BOLS correlation theory formulates [35,36]:

$$\begin{cases} C_z = 2 \left\{ 1 + \exp \left[\frac{12 - z}{8z} \right] \right\}^{-1} \\ C_z^{-m} = \frac{E_z}{E_b} = 1 + \Delta H' \end{cases} \quad (1)$$

The parameter m is the bond nature indicator of a specific material, which is not freely adjustable. Exercises [37] have verified that $m = 1$ for elemental metals and $m = 2.56$ [38] and 4.88 [39] for carbon and silicon, respectively. The subscript z is the effective coordination number (CN), which is determined by the atomic layer and the crystal registry:

$$\begin{cases} Z_1 = \begin{cases} 4(1 - 0.75/K) & \text{Curved surface} \\ 4 & \text{Flat surface} \end{cases} \\ Z_2 = Z_1 + 2 \\ Z_3 = 8 \text{ or } 12 \end{cases} \quad (2)$$

where K is the dimensionless form of size, which is the number of atoms lined along the radius of a spherical dot, a rod, or across the thickness of a thin plate.

According to the energy band theory and the BOLS notion [33,40], in the interface region, bond order distortion and bond nature alteration perturbs the single-body Hamiltonian with charge entrapment or polarization, which is expressed as:

$$\begin{aligned} H &= -\frac{\hbar^2 \nabla^2}{2m} + V_{atom}(r) + V_{cryst}(r, I) \\ &= -\frac{\hbar^2 \nabla^2}{2m} + V_{atom}(r) + V_{cryst}(r, B)(1 + \Delta H') \end{aligned} \quad (3)$$

where the intra-atomic trapping potential, $V_{atom}(r)$, determines the specific v th energy level of an isolated atom, $E_v(0)$, from which the binding energy (BE) starts to shift upon the crystal potential $V_{cryst}(r)$ being involved. $\Delta H'$ is the perturbation. The parameters I and B denote the interface and the bulk, respectively. Only the $V_{cryst}(r)$ can be perturbed but the $V_{atom}(r)$ is intrinsically unchangeable.

2.2. Atomic binding energy and its bulk shift

The interface energetics plays a key role in interface because the interface energetics links directly the microscopic bonding configuration to its macroscopic properties, such as strength, elasticity, reactivity, diffusivity, stability, etc. The interfacial energy is the energy consumed to create per unit area of surface. However, we argue that the energy stored per unit volume at the interface region could be more meaningful than the energy per unit area, as energy is always a volume-related quantity. So, herewith, we focus on the interfacial atomic cohesive energy and the energy density.

To obtain the interfacial adhesion energy that is the energy per unit area, we need to determine first the binding energy of an isolated constituent atom in the hetero-interface region. On the basis of the tight-binding (TB) approach [40], the energy shift of a specific v th core band from the $E_v(0)$ of an isolated atom is proportional to the bond energy at equilibrium:

$$\begin{aligned} \Delta E_v(z) &= E_v(z) - E_v(0) = \Delta E_v(B)(1 + \Delta H') \\ &= (\alpha + z\beta)(1 + \Delta H') \end{aligned} \quad (4)$$

where

$$\begin{cases} \Delta E_v(B) = E_v(B) - E_v(0) = (\alpha + z\beta) \propto \langle E_b \rangle & \text{Bulk shift} \\ E_v(0) = -\langle v, i | V_{atom}(r) | v, i \rangle & \text{Isolated atomic core level} \\ \alpha = -\langle v, i | V_{cryst}(r, B)(1 + \Delta H') | v, i \rangle \propto \langle E_i \rangle & \text{Exchange integral} \\ \beta = -\langle v, i | V_{cryst}(r, B)(1 + \Delta H') | v, i \rangle \propto \langle E_i \rangle & \text{Overlap integral.} \end{cases} \quad (5)$$

$E_v(z)$ is the specific v th energy level of an atom with z coordination number and $\Delta E_v(z) = E_v(z) - E_v(0)$ is the shift; the $\Delta E_v(B)$ or $z = 12$ is the shift of the ideal bulk; α and β represent the potential of exchange integral and overlap integral, respectively, and $\alpha \gg \beta$. Therefore, Eq. (4) turns:

$$\frac{E_v(z) - E_v(0)}{E_v(B) - E_v(0)} = 1 + \Delta H' = C_i^{-m} \quad (6)$$

The zone-selective photoelectron spectroscopy (ZPS) [41] constrains the relative shift of each component:

$$\begin{aligned} \frac{E_v(z) - E_v(0)}{E_v(z') - E_v(0)} &= \frac{C_z^{-m}}{C_{z'}^{-m}} \quad \text{or} \\ \frac{E_v(z) - E_v(B)}{E_v(z') - E_v(B)} &= \frac{C_z^{-m} - 1}{C_{z'}^{-m} - 1} \quad (z \neq z') \end{aligned} \quad (7)$$

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